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(54) **LITHIUM BATTERY PACKAGING LAMINATED MULTILAYER STRUCTURE**
MULTISCHICHT-VERBUNDSTRUKTUR ZUM PACKEN EINER LITHIUMZELLE
MATERIAU MULTICOUCHES STRATIFIÉ D'ENVELOPE DE PILE AU LITHIUM

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Description

[0001] The present invention relates to a Lithium battery packaging laminated structure resistant to acids and organic solvents. Generally, batteries, such as lithium batteries, include those using a liquid electrolyte, those using a gelled electrolyte and those using a solid electrolyte. Lithium batteries include lithium ion batteries and polymer batteries.

[0002] Various pouches formed by working various laminated structures each formed by laminating various kinds of sheets are used principally as packaging articles. Recently, lithium batteries each formed by packaging a lithium battery module in a pouch formed from a laminated structure have been developed.

[0003] A lithium battery module, which is also called a lithium secondary battery module, employs a polyelectrolyte, generates current by the agency of the migration of lithium ions and have positive and negative electrodes containing polymers as active substances.

[0004] The lithium battery comprises a lithium battery module having a positive electrode collector (aluminum or nickel), a positive electrode active substance layer (metal oxide, carbon black, a metal sulfide, an electrolytic solution or a polymer, such as polyacrylonitrile), an electrolytic layer (a carbonate electrolytic solution of propylene carbonate, ethylene carbonate, dimethyl carbonate or ethylene methyl carbonate, an inorganic solid electrolyte of a lithium salt or a gelled electrolyte), a negative electrode active layer (lithium, an alloy, carbon, a liquid electrolyte or a polymer, such as polyacrylonitrile) and a negative collector (copper, nickel or a stainless steel), and a package containing the lithium battery module therein.

[0005] The lithium battery is used as a power supply for personal computers, portable terminal devices, such as portable telephones and PDAs, video cameras, electric vehicles, robots, artificial satellites and the like and as an energy storage battery.

[0006] The lithium battery comprises a lithium battery module having a positive collector of aluminum or nickel, a positive electrode active substance layer of a metal oxide, carbon black, a metal sulfide, an electrolytic solution or a polymer, such as polyacrylonitrile, an electrolytic layer of a carbonate electrolytic solution of propylene carbonate, ethylene carbonate, dimethyl carbonate, ethyl carbonate or ethylene methyl carbonate, an inorganic solid electrolyte containing a lithium salt or a gelled electrolyte, a negative electrode active layer of lithium, an alloy, carbon, a liquid electrolyte or a polymer, such as polyacrylonitrile, and a negative collector of copper, nickel or a stainless steel, and a package containing the lithium battery module therein.

[0007] The package of the lithium battery is a cylindrical or parallelepipedic metal can formed by pressing a metal sheet or a pouch formed by working a multilayer film consisting of an outer layer, an aluminum layer and a sealant layer.

[0008] These packages for the lithium batteries have the following problems. The metal can has rigid walls and hence the shape of the lithium battery module is dependent on that of the metal can. Since the hardware is designed so as to conform to the shape of the battery pack, the dimensions of the hardware are dependent on the shape of the battery pack, which reduces the degree of freedom of designing the shape of the hardware.

[0009] The pouch made from a multilayer film does not place any restrictions on the shape of the hardware using the battery pack like the metal can does. However, there have not yet been developed any packaging laminated structures satisfactorily meeting physical properties and functions required of materials of packages for the lithium battery. The required physical properties and functions include the followings.

[0010] For example, the package for the lithium battery must be capable of hermetically sealing portions of electrodes connecting a principal part of the lithium battery module to hardware to insulate the same from the atmosphere. Therefore, the innermost layer of the multilayer film must be capable of adhering to the electrodes, particularly, must be capable of adhering to the electrodes when heat and pressure are applied thereto.

[0011] The lithium battery must be capable of maintain the sealing effect even if the temperature of the lithium battery module rises during charging and discharging, and must be, as well as hardware that withstands high temperatures, such as high temperatures on the instrument panel of a vehicle in summer, and low temperatures in a cold district, must be heat-resistant and cold-resistant. The lithium battery must be capable of maintaining satisfactory sealing effect in a severe environment.

[0012] Sometimes, it occurred that the electrolyte of the lithium battery module consisting of a carbonate solvent and a lithium salt affects adversely to the package and reduces bond strength between the layers of the multilayer film. The solvent (carbonate solvent) contained in the lithium battery module swells adhesive layers bonding together the component layers of the multilayer film to reduce bond strength between the layers.

[0013] It is possible that an acid is produced and heat is generated by the hydrolysis of the electrolyte, a metal barrier layer is corroded by the agency of the acid and heat to reduce bond strength between the layers, and that the battery is ignited by the heat. If the temperature of the battery rises, the electromotive force of the battery decreases and it is possible that the device connected to the battery stops or malfunctions.

[0014] The electrolysis of the electrolyte that causes those problems is caused by the penetration of external moisture into the sealed system of the battery. Therefore, the package must have a barrier property capable of inhibiting the penetration of external moisture into the package.

[0015] Packages containing batteries including lithium batteries must not be conductive and must not transmit electricity to devices (hardware) surrounding the pack-

ages and must be capable of electrically isolating the electrodes from each other so that the electrodes are not short-circuited.

[0016] The package of the lithium battery may be a metal can, a pouch or a formed package having a container and a cover. When the formed package having the containing part and the cover is employed, a resin forming the innermost layer of the laminated structure must be heat-adhesive and the laminated structure for forming the formed package must have a high formability.

[0017] JP-A-10 208 708 describes flat cell. JP-A-1 167 166 describes an image forming device. WO 99/36971 A describes a battery package comprising a battery, a pouch which encloses said battery, and separating means.

[0018] The present invention has been made in view of those problems and it is therefore an object of the present invention to provide a battery packaging laminated structure excellent in gas-barrier property, having high mechanical strengths including piercing strength and capable being used in a hot environment and stable under the influence of an electrolyte.

[0019] According to the present invention, there is provided a lithium battery packaging laminated structure for forming into a battery poach or an embossed battery package comprising:

> an outermost layer, a barrier layer and an innermost layer laminated in that order;
> wherein
> the outermost layer is formed of an insulating resin, has a thickness of at least 6 μm, and is bonded to the barrier layer by dry lamination using a bonding film or by extrusion coating,
> the barrier layer is a soft aluminum foil having an iron content in the range of 0.3 to 9.0%,
> the innermost layer is a multilayer film consisting of at least two resin films, one of the resin films on the side of the barrier layer including an unsaturated carboxylic acid graft polyolefin resin, and
> the barrier layer has a surface on the side of the innermost layer coated with an acid-resistant film of a phosphate or a chromate, or coated with a protective layer.

[0020] Preferably, a surface of the aluminum fail of the barrier layer on the side of the innermost layer is finished by degreasing or pickling.

[0021] Preferably, the barrier layer has a surface on the side of the innermost layer, coated with a 0.5 to 30 μm thick protective layer of a resin containing 30% or above of at least one of epoxy resins, phenol resins, melamine resins, polyimide resins, unsaturated polyester resins, polyurethane resins, alkyd resins, unsaturated carboxylic acid graft polyolefin resins, polyester copolymers, such as polyethylene terephthalate resins or polybutylene terephthalate resins, ionomers, ethylene-vinyl acetate copolymers, copolymers of ethylene and an acrylic acid derivative, copolymers of ethylene and a methacrylic acid derivative, polyether resins and derivatives of those resins.

[0022] Preferably, the innermost layer has a thickness of 10 μm or above and is formed of one of unsaturated carboxylic acid graft polyolefin resins including unsaturated carboxylic acid graft polyethylene resins, unsaturated carboxylic acid graft polypropylene resins, unsaturated carboxylic acid graft poly(methyl pentene) resins and mixtures of some of those resins, and having a melting point of 80 °C or above and a vicat softening point of 70 °C or above.

[0023] Preferably, at least one dry lamination adhesive layer of a dry lamination adhesive is formed between the layers on the side of the innermost layer with respect to the barrier layer, the dry lamination adhesive includes a resin and an accelerator, the resin is a blended resin of a polyester resin consisting of an acid component containing at least two of sebacic acid, isophthalic acid, terephthalic acid, octanedioic acid, nonanedioic acid, undecanedioic acid and palmitic acid, and an alcohol component containing at least one of ethylene glycol, hexanediol and glycol, and a bisphenol A-type epoxy resin, and the accelerator contains a polyisocyanate component.

[0024] Preferably, the innermost layer is a multilayer film consisting of at least two resin films formed by coextrusion, and one of the resin films cannot be welded to metal members but the same resin film is heat-adhesive.

> Fig. 1 is a view of a battery packaging laminated structure embodying the present invention;
> Fig. 2 is a view of a battery packaging structure in a modification of the battery packaging laminated structure embodying the present invention;
> Fig. 3 is a sectional view of a battery packaging laminated structure;
> Fig. 4 is a view showing a battery pouch and tabs bonded to the battery pouch;
> Fig. 5 is a view showing battery pouches;
> Fig. 6 is a view of a battery pouch in a modification of the above battery pouch;

[0025] The lithium battery packaging laminated structure according to the present invention will be described with reference to the accompanying drawings.

[0026] Figs. 1(a) to 1(d) show a lithium battery packaging laminated structure in a first example, in which Fig. 1(a) is a typical sectional view of a basic laminated structure, Fig. 1(b) is a perspective view of assistance in explaining a lithium battery, Fig. 1(c) is a sectional view taken on line X_1-X_1 in Fig. 1(b), and Fig. 1(d) is a sectional view taken on line X_2-X_2 in Fig. 1(b). Figs. 2(a) to 2(d) show a lithium battery packaging laminated structure in a second example, in which Fig. 2(a) is a typical sectional view of a basic laminated structure, Fig. 2 (b) is a perspective view of assistance in explaining a lithium battery, Fig. 2(c) is a perspective view of a lithium battery provided with an embossed battery package and Fig. 2(d) is a

sectional view taken on line X_3-X_3 in Fig. 2(c). Fig. 3 is a sectional view of a battery packaging laminated structure in a third example according to the present invention for packaging a lithium battery module. Figs. 4 (a) to 4 (e) show another package according to the present invention and tabs, in which Fig. 4(a) is a perspective view of a lithium battery, Fig. 4(b) is a perspective view of a lithium battery module with tabs bonded thereto, Fig. 4 (c) is a perspective view of another lithium battery module provided with heat-adhesive tabs bonded thereto, and Figs. 4(d) and 4(e) are sectional views taken on line X_4-X_4 in Fig. 4 (a) . Figs. 5(a) to 5(e') are plan views and sectional views of battery pouches formed from a lithium battery packaging laminated structure according to the present invention. Figs. 6(a) to 6(d) are views of an embossed lithium battery package formed from a lithium battery packaging laminated structure according to the present invention, in which Fig. 6(a) is a perspective view of a container of a single-part embossed battery package, Fig. 6(a') is a sectional view taken on line X_9-X_9 in Fig. 6(a), Fig. 6(b) is a perspective view of a double-part embossed battery package, Fig. 6(b') is a sectional view taken on line X_{10}-X_{10} in Fig. 6 (b) , Fig. 6(c) is a perspective view showing tabs of an embossed battery package and Fig. 6(d) is a conceptional perspective view showing tabs of another embossed battery package.

[0027] The inventors of the present invention found through the earnest study of problems to be solved by the present invention that the problems can be solved by a laminated structure 10 shown in Fig. 1(a) and have made the present invention. As shown in Figs. 1(b) and 1(c), a lithium battery 1 related with the present invention is formed by sealing a lithium battery module 2 having terminals 3 in a pillow type battery package (battery pouch)4 having a back sealed part 5f with the terminals 3 partly extending outside the battery package 4.

[0028] As shown in Figs. 2(b) and 2(d), an embossed battery package (sometimes, referred to as "cup-type battery package") has a container 6 having an embossed part 8 and a flange 9, and a cover 7 formed by cutting the laminated structure 10. The container 6 is formed by press forming (embossing) the laminated structure 10, a lithium battery module 2 is put in the embossed part 8 of the container 6, and the cover 7 is put on the flange 9 of the container 6 so as to cover the lithium battery module 2, and a peripheral part of the cover 7 is bonded to the flange 9 of the container 6 by heat-sealing to seal the lithium battery in the embossed battery package.

[0029] The battery pouch and the embossed battery package will be described in detail later.

[0030] Basically, the laminated structure 10 has an outermost layer 11, a barrier layer 12 and an innermost layer 14 laminated in that order. An intermediate layer may be sandwiched between the barrier layer 12 and the innermost layer 14. Fig. 1(a) shows a laminated structure 10 having an outermost layer 11, a barrier layer 12 an intermediate layer 13 and an innermost layer 14 laminated in that order. Those component layers of the laminated structures 10 are formed of the following materials. As shown in Fig. 1(d), a lithium battery relating with the present invention has a heat-sealed part 5 including portions of the terminals 3.

[0031] The outermost layer 11 of the laminated structure according to the present invention is formed of an oriented polyester resin or an oriented nylon resin. Possible polyester resins are polyethylene terephthalate resins, polyethylene naphthalate resins, polyethylene naphthalate resins, polyester copolymers, polycarbonate resins and the like. Possible nylons are crystalline or non-crystalline nylons including nylon 6, nylon 66, copolymers of nylon 6 and nylon 66, nylon 610, polymethaxylilene adipamide (MXD6).

[0032] When the lithium battery is used on a device (hardware), the outermost layer 11 touches the device. Therefore, it is desirable to form the outermost layer 11 of an insulating resin. Since a film forming the outermost layer 11 has pinholes and pinholes will be formed in the film during processing, the thickness of the outermost layer 11 must be 6 μm or above preferably, the thickness of the outermost layer 11 is in the range of 12 to 25 μm.

[0033] The outermost layer 11 may be formed from a laminated film in view of providing the outermost layer 11 with a high pinhole-resistant property and an improved insulating ability.

[0034] Preferably, the outermost layer 11 includes at least one resin layer consisting of two or more layers each having a thickness of 6 μm or above, preferably, in the range of 12 to 25 μm. The following laminated structures 1) to 3) are examples of the outermost layer 11 of laminated construction.

1) oriented polyethylene terephthalate film/ON
2) Oriented polyethylene terephthalate film/Polyethylene film
3) ON/Polyethylene film

[0035] The outermost layer 11 is bonded to the barrier layer 12 by dry lamination using a bonding film or by extrusion coating.

[0036] The barrier layer 12 prevents the penetration of moisture into the lithium battery 1. To avoid the adverse effect of pinholes that may be formed in the barrier layer 12, to stabilize the workability (ease of fabricating pouches or forming) and to provide the barrier layer 12 with pinhole resistance, the barrier layer 12 is formed from a foil of aluminum. Preferably, the thickness of the barrier layer 12 is in the range of 20 to 80 μm.

[0037] The inventors of the present invention made earnest studies to reduce pinholes and to prevent the formation of cracks in an embossed battery package and found that aluminum having an iron content in the range of 0.3 to 9.0%, preferably, in the range of 0.7 to 2.0% is superior in ductility to aluminum not containing any iron, pinholes are less liable to be formed in a film of such aluminum when a laminated structure including the film of such aluminum is folded and walls of an embossed

battery package can be easily formed. Aluminum having an iron content less than 0.3% is unable to form a satisfactorily pinhole-resistant film and does not have improved formability. Aluminum having an iron content exceeding 9.0% is unsatisfactory in flexibility and affects adversely to the workability of the laminated structure in forming a pouch.

[0038] The inventors of the present invention found that coating a surface of an aluminum film with an acid-resistant film TR and a protective layer 15 and employment of the foregoing techniques have remarkable effect on preventing the dissolution and corrosion of the surface of the aluminum foil by hydrofluoric acid (HF) produced by the interaction of the electrolyte of the lithium battery module 2 and moisture, improving the adhesive property (wettability) of the surface of the aluminum foil and stabilizing the adhesive strength between the aluminum foil and the innermost layer.

[0039] The acid-resistant film TR formed on the aluminum foil is a film of a phosphate or a chromate. The phosphate is zinc phosphate, iron phosphate, manganese phosphate, calcium phosphate or chromium phosphate. The chromate is chromium chromate.

[0040] The adhesive property of the surface of the aluminum foil can be improved by finishing the surface by a coupling property improving process and/or surface roughening. The coupling property improving process may use a silane coupling agent, an organic titanium coupling agent or an organic aluminum coupling agent.

[0041] An organic titanium coupling agent may be tetraalkoxy titanium, titanium acylate, titanium chelate or the like. The organic aluminum coupling agent may be trialkoxy aluminum, aluminum chelate, aluminum acylate or the like.

[0042] Surface roughening of the aluminum foil is effective in improving the adhesive property of the surface of the aluminum foil. The surface of the aluminum foil may be etched and cleaned with an acid or alkali solution to remove aluminum oxide (Al_2O_3) formed on the surface of the aluminum foil, to increase surface area by enhancing the surface roughness and to provide the surface with an anchoring property for the improvement of adhesive property.

[0043] The protective layer 15 formed on the surface of the aluminum foil is a layer of a resin, such as an epoxy resin, a phenolic resin, a melamine resin, a polyester resin, an unsaturated carboxylic acid graft polyolefin resin or a derivative of one of those resins, containing a modifier for acid resistance improvement.

[0044] The foregoing surface treatment processes may be used in combination.

(1) Aluminum barrier layer 12/Formation of acid-resistant film TR
(2) Aluminum barrier layer 12/Formation of acid-resistant film TR/Formation of protective layer 15

[0045] According to the present invention, a second protective layer 15a of a resin not containing any modifier for acid resistance improvement may be formed in addition to the protective layer 15 containing a modifier for acid resistance improvement. The second protective layer 15a may be formed of an epoxy resin, a phenolic resin, a melamine resin, an olefin resin, an unsaturated carboxylic acid graft polyolefin resin, an acrylic resin or a derivative of one of those resins.

[0046] The second protective layer 15a is formed, for example, by either of the following methods.

(1) Aluminum barrier layer 12/Formation of acid-resistant film TR/Formation of second protective layer 15a
(2) Aluminum barrier layer 12/Formation of acid-resistant film TR/Formation of protective layer 15/Formation of second protective layer 15a

[0047] According to the present invention, an intermediate layer 13 may be sandwiched between the barrier layer 12 or the protective layer 15, and the innermost layer 14 by using films for dry lamination DL or thermal lamination TL. The intermediate layer 13 protects the barrier layer 12 and prevents contact (short circuit) between the terminals 3 and the aluminum barrier layer 12 due to the thinning of the innermost layer 14, i.e., a heat-adhesive layer, by heat and pressure applied thereto in a heat-sealing process for forming a pouch. The intermediate layer 13 may be formed by bonding together a first intermediate layer 13a and a second intermediate layer 13b by a film for dry lamination DL.

[0048] The intermediate layer 13 is added to stabilize the environmental suitability (heat resistance and cold resistance) of the lithium battery. The intermediate layer 13 has a thickness of 10 μm or above and a melting point of 80 °C or above. Preferably, the intermediate layer 13 includes at least one layer of a thickness in the range of 12 to 25 μm formed of a polyester resin, a polyolefin resin, a derivative of one of those resins or a resin produced by mixing some of those resins.

[0049] Suitable polyester resins for forming the intermediate layer 13 are polyethylene terephthalate resins, polybutylene terephthalate resins, polyethylene naphthalate resins, polybutylene naphthalate resins, polycarbonate resins, copolymers of some of those polymers and derivatives of those polymers. The polyolefin resins are polypropylene resins, ethylene-propylene copolymers, low-density polyethylene resins, medium-density polyethylene resins, high-density polyethylene resins, linear low-density polyethylene resins, ethylene-α-olefin copolymers produced through polymerization using a single-site catalyst, polyethylene resins containing metal ions, copolymers of ethylene and acrylic acid derivatives, copolymers of ethylene and methacrylic acid derivatives, polybutene resins, unsaturated carboxylic acid graft poly (methyl pentene) resins and derivatives of those polymers.

[0050] Films of these resins may be either oriented or

unoriented.

[0051] The innermost layer 14 of the lithium battery packaging laminated structure according to the present invention is bonded to the intermediate layer 13 by a film for dry lamination DL. The innermost layer 14 is formed of an unsaturated carboxylic acid graft polyolefin resin, a copolymer of ethylene and an acrylic acid derivative or a copolymer of ethylene and a methacrylic acid derivative, a metal ion crosslinked polyethylene resin, a derivative of some of those polymers or a mixture of some of those polymers. Preferably, the innermost layer 14 has a thickness of 20 μm or above and is formed of a resin having a melting point of 70 °C or above and a Vicat softening point of 60 °C or above.

[0052] An innermost layer 14' of a polyolefin resin not adhesive to metals may be used. When the innermost layer 14' is used, the terminals 3 are covered with heat-adhesive tabs 16 of 15 μm or above in thickness formed of unsaturated carboxylic acid graft polyolefin, metal ion crosslinked polyethylene, a copolymer of ethylene or propylene and acrylic acid, or a copolymer of propylene and acrylic acid, methacrylic acid or a methacrylic acid derivative. The tabs 16 can be perfectly hermetically bonded to the innermost layer 14' as shown in Fig. 4. More concretely, portions of the terminals 3 of a lithium battery module 2 to be packaged in a battery package are sandwiched between heat-adhesive tabs 16 of a width greater than that of the terminals 3 as shown in Fig. 4 (b), the lithium battery module 2 is put in the battery package, and the battery package is sealed. Fig. 4(d) is a typical sectional view taken on line X_4-X_4 in Fig. 4(a). In Fig. 4 (d), the outermost layer 11, the barrier layer 12, and the intermediate layer 13 are represented by a single layer. Fig. 4(c) shows a lithium battery module 2 provided with terminals 3 having portions wrapped in heat-adhesive tabs 16 to be covered with the battery package. Fig. 4(e) is a typical sectional view taken on line X_4-X_4 in Fig. 4(a) when the lithium battery module 2 shown in Fig. 4(c) is sealed in the battery package.

[0053] In the lithium battery 1 using a pouch or an embossed battery package, the terminals of a lithium battery module are sandwiched between the innermost layers 14 and the innermost layers 14 are welded together to form a sealed system. However, welded portions of the olefin resin forming the innermost layers becomes brittle and cracks and pinholes are liable to be formed therein. The thickness of the innermost layer is reduced by a value corresponding to the thickness of the tabs 16 when the innermost layers are welded to the tabs 16 to prevent forming pinholes. If the innermost layer is formed of a single layer of an olefin resin having a high melting point to enhance the heat resistance of the innermost layer, a high pressure and heat of a high temperature must be applied for a long time to the innermost layers to weld the innermost layers together by heat-sealing. Such a welding process deteriorates the characteristic of the lithium battery module 2 and deteriorates the function of the battery package by causing the shrinkage of the other component layer, such as the outermost layer of a polyester resin or a nylon resin, by heat.

[0054] The inventors of the present invention made studies to solve such a problem and found that it is effective in solving such a problem to form the innermost layer 14 in a multilayer structure consisting of a first layer 14a on the side of the inner surface of the laminated structure 10 and a second layer 14b on the side of the outer surface of the laminated structure 10. More concretely, the following multilayer structures can be used as the innermost layer.

(1) Film of an olefin resin or a derivative of olefin resin/Unsaturated carboxylic acid graft polyolefin film
(2) Film of an olefin resin or a derivative of an olefin resin/Film of a copolymer of ethylene and an acrylic acid derivative or a copolymer of ethylene and a methacrylic acid derivative
(3) Film of an olefin resin or a derivative of olefin resin/Metal ion crosslinked polyethylene or metal ion crosslinked polypropylene film

[0055] The following are representative olefin resins.

a) Polypropylene resins

1) Homopolypropylene (melting point: 150 °C or above, vicat softening point: 140 °C or above)
2) Ethylene-propylene copolymer (terpolymer of random propylene, block propylene or butene-random propylene copolymer having a melting point of 110 °C or above and a Vicat softening point of 100 °C or above)

b) polyethylene resins

1) Low-density polyethylene, medium-density polyethylene, high-density polyethylene, linear low-density polyethylene, ethylene-propylene-diene copolymer ethylene-propylene-butene copolymer and ethylene-α-olefin copolymer produced through polymerization using a single-site catalyst (melting point: 90 °C or above, Vicat softening point: 80 °C)

[0056] Acid-denatured polyolefin resins (melting point: 90 °C or above, Vicat softening point: 80 °C)

a) Ethylene-vinyl acetate copolymers
b) Metal ion crosslinked polyethylene, metal ion crosslinked polypropylene
c) Unsaturated carboxylic acid graft polyolefins including unsaturated carboxylic acid graft polyethylene, unsaturated carboxylic acid graft polypropylene and unsaturated carboxylic acid graft poly(methyl pentene), and derivatives of those polymers
d) Copolymers of ethylene or propylene, and meth-

acrylic acid derivatives or acrylic acid derivatives, including ethylene-methyl methacrylate copolymers (EMMA), ethylene-ethyl methacrylate copolymers (EMA), ethylene-methyl acrylate copolymers (EMAA), ethylene-ethyl acrylate copolymers (EEA), ethylene-acrylate copolymers (EAA), propylene-ethyl methacrylate (PMA) and propylene-ethyl acrylate (PAA)

[0057] The following multilayer structures may be used as the multilayer innermost layer 14.

(1) Low-density polyethylene or linear low-density polyethylene/Copolymer of ethylene and a methacrylic acid derivative or an acrylic acid derivative
(2) Ethylene-propylene copolymer/Copolymer of propylene and a methacrylic acid derivative or an acrylic acid derivative
(3) Low-density polyethylene or linear low-density polyethylene/Metal crosslinked polyethylene
(4) Ethylene-propylene copolymer/Metal crosslinked propylene
(5) Random propylene/Unsaturated carboxylic acid graft homopropylene
(6) Block propylene/Unsaturated carboxylic acid graft homopropylene
(7) Homopropylene/Unsaturated carboxylic acid graft random or graft propylene
(8) Random or block propylene/Homopropylene
(9) Ethylene-propylene copolymer/Polyethylene/ethylene-propylene copolymer
(10) Ethylene-propylene copolymer/Polyethylene/Unsaturated carboxylic acid graft polyethylene
(11) Homopropylene/Random propylene
(12) Random polypropylene/Homopropylene/random propylene
(13) Random propylene/Block propylene/Random propylene
(14) Random propylene/Butene-random propylene copolymer
(15) Homopropylene/Butene-random propylene copolymer

[0058] It is desirable that the innermost layer 14 has a coefficient of static friction and a coefficient of kinetic friction of 0.5 or below, preferably, 2.0 or below to stabilize embossing formability. To form the innermost layer 14 having such a coefficient of friction, it is preferable that the material forming the innermost layer 14 contains 500 ppm or above of a fatty acid amide lubricant, such as erucic acid amide, stearic acid amide or oleic acid amide, or 1000 ppm or above of silicone lubricant having a molecular weigh of 100,000 or above, such as dimethyl silicone or methyl phenyl silicone, or 3% or above of silicone resin powder.

[0059] The component layers of the laminated structure 10, i.e., the lithium battery packaging laminated structure according to the present invention, may be processed by a surface activating process, such as a corona discharge process, a blasting process, an oxidizing process or an ozonation process, to stabilize properties needed for film formation, lamination and final product forming (embossing or pouch fabrication).

[0060] The outermost layer 11 and the barrier layer 12 of the laminated structure or the outermost layer 11, the barrier layer 12, the intermediate layer 13 and the innermost layer 14 may be formed and laminated by a T-die extrusion coating process, a tubular film extrusion process or a coextrusion process. When necessary, a secondary film may be formed by a coating process, an evaporation process, an ultraviolet curing process or an electron beam curing process. The adjacent layers may be bonded together by a dry lamination process, an extrusion coating process, a coextrusion lamination process or a thermal lamination process. The layers on the outer side of the barrier layer 12 may be laminated by a dry lamination process using an ordinary adhesive for dry lamination. Preferably, adhesives of compositions, which will be described below, are used for laminating the layers on the inner side of the barrier layer 12.

[0061] When the laminated structure for forming a lithium battery package is formed by a dry lamination process, it is possible that the layers are separated by the agency of a polycarbonate solvent contained in the electrolyte of the lithium battery module and the layer bonded to the inner surface of the barrier layer 12 is separated by the agency of hydrofluoric acid produced by the interaction of the lithium salt and water. The inventors of the present invention found through earnest studies that the separation of the layers and the separation of the layer from the surface of the barrier layer can be prevented and a laminated structure having excellent heat resistance can be formed by laminating the layers on the inner side of the barrier layer 12 of the laminated structure 10 by dry lamination using an adhesive of the following composition.

[0062] The adhesive is a two-part adhesive supplied in a resin and an accelerator. The resin is a blended resin of a polyester resin consisting of an acid component containing at least two of sebacic acid, isophthalic acid, terephthalic acid, octanedioic acid, nonanedioic acid, undecanedioic acid and palmitic acid, and an alcohol component containing at least one of ethylene glycol, hexanediol and diethylene glycol, and a bisphenol A-type epoxy resin. The accelerator contains a polyisocyanate component (TDI, MDI, IPDI, FDI or ADI).

[0063] When unsaturated carboxylic acid graft polyolefin is used as a resin for extrusion coating or thermal lamination, adhesive strength and chemicals unsusceptibility, i.e., resistance to the adverse effect of chemicals, are improved.

[0064] When layers are laminated by extrusion coating, the adhesive strength between the layers can be stabilized by an adhesive strength enhancing process that coats the bonding surface of the layer to be bonded to another with an about 1 μm thick film of any one of

polyester resins, polyether resins, urethane resins, polyether-urethane resins, polyester-urethane resins, isocyanate resins, polyolefin resins, polyethylene-imine resins, cyanoacrylate resins, organotitanium compounds, epoxy resins, imide resins, silicone resins, derivatives of those resins and mixtures of some of those resins or by a surface activation process, such as an ozonation process.

[0065] The following are three representative methods of forming the laminated structure 10 of the present invention consisting of the three layers.

1) A method that forms a laminated structure of the outermost layer 11 and the barrier layer 12 as a first substructure, and the innermost layer 14 as a second substructure separately, and laminates the first and the second substructures by thermal lamination.
2) A method that forms a laminated structure of the outermost layer 11 and the barrier layer 12 as a first substructure, and the innermost layer 14 as a second substructure separately, and laminates the first and the second substructures by extrusion coating (or coextrusion lamination). When necessary, the laminated structure is subjected to a thermal lamination process.
3) A method that laminates the outermost layer 11, the barrier layer 12 and the innermost layer 14 by dry lamination.

[0066] The following are three representative methods of forming the laminated structure 10 of the present invention consisting of the four layers.

1) A method that forms a laminated structure of the outermost layer 11 and the barrier layer 12 as a first substructure, and a laminated structure of the intermediate layer 13 and the innermost layer 14 as a second substructure separately, and laminates the first and the second substructures by thermal lamination.
2) A method that forms a laminated structure of the outermost layer 11 and the barrier layer 12 as a first substructure, and a laminated structure of part of the intermediate layer 13 and the innermost layer 14 or only the innermost layer 14 as a second substructure separately, and laminates the first and the second substructures by extruding the intermediate layer 13 for extrusion coating (or coextrusion lamination). When necessary, the laminated structure is subjected to a thermal lamination process.
3) A method that laminates the outermost layer 11, the barrier layer 12, the intermediate layer 13 and the innermost layer 14 by dry lamination.

[0067] The intermediate layer 13 may be coated with a thin film impermeable to gases, liquids and ions to prevent the permeation of the components of the electrolyte through the barrier layer 12 and to secure stable adhesive strength. The thin film may be a metal thin film, such as an aluminum film, or a metal oxide film, such as an aluminum oxide or a tin oxide film, formed by a sputtering process, a chemical vapor deposition process or a physical vapor deposition process or a resin film, such as a vinylidene chloride film, formed by a coating process.

Examples

[0068] Laminated structures in examples of the laminated structure 10 according to the present invention as the lithium battery packaging laminated structure were fabricated and pouches and embossed battery packages for packaging a lithium battery module were formed from the laminated structures. The quality and performance of the laminated structures, the pouches and the embossed battery packages were evaluated.

[0069] In the following description, materials of films and processes will be represented by the following symbols (acronyms, initial words and abbreviations).

Symbols

[0070] PET: Polyester film, CPET: Copolyester film, OPET: Oriented polyester film, ON: Oriented polyamide (nylon) film, NY: Polyamide (nylon) film, P-EP: Epoxy protective layer, AL: Aluminum foil, COPET: Oriented copolyester film, PC: Chromium phosphate film, 3C: Tervalent chromium film, PZ: Zinc phosphate film, PCa: Calcium phosphate film, PUD: Polyester-urethane adhesive film, PED: Polyether-urethane adhesive film, PAD: Unsaturated carboxylic acid graft random polypropylene adhesive film, PEAD: Unsaturated carboxylic acid graft polyethylene adhesive film, TL: Thermal lamination, DL: Dry lamination, EC: Extrusion lamination, ANC: Anchor coat, EP: Epoxy resin film, FN: Phenolic resin film, MR: Melamine resin film, AC: Acrylic resin film, PPA: Unsaturated carboxylic acid graft random polypropylene film (unsaturated carboxylic acid graft polypropylene film), PEA: Unsaturated carboxylic acid graft polyethylene film, EAM: Ethylene-methyl methacrylate copolymer film, PH: Homopolypropylene film, PR: Random polypropylene film, PP: Polypropylene film, BR: Butene-random propylene copolymer film, PE: Polyethylene film, HD: High-density polyethylene film, LD : Low-density polyethylene film, MD: Medium-density polyethylene film, AD: Acid-modified unsaturated polyolefin film, PMa: Unsaturated carboxylic acid graft poly(methyl pentene) film, TPX: Poly (methyl pentene) film.

[0071] Unless otherwise specified, the dry lamination process used a polyester-urethane adhesive for lamination.

Evaluation

[0072] Pouches and embossed battery packages were fabricated and abilities of the pouches and embossed battery packages were evaluated for the following prop-

erties.

1. Electrolyte Resistance

[0073] An imitation electrolyte was poured into a test sample, the test sample was sealed. The condition of adhesion between the barrier layer 12 and the innermost layer 14 or between the barrier layer 12 and the intermediate layer 13 was examined after storing the test sample at 60 °C for thirty days.

2. Moisture Impermeability

[0074] Moisture content of a test sample was measured after storing the test sample in an environment of 40 °C and 90% RH for thirty days. The moisture content must be 300 ppm or below.

3. Change in Peel Strength of the Innermost Layer

[0075] Peel strength of the innermost layer was measured after storing the test sample in an environment of -40 °C for thirty days and leaving the same at a room temperature (23 °C) for one hour. The peel strength must be 9.8 N/ 15 mm (1 kgf/15 mm) or above.

4. Short Circuit Preventing Ability

[0076] The terminals 3 covered with the tabs 16 were sandwiched between the innermost layers 14 and portions of the innermost layers 14 holding the portions of the terminals covered with the tabs 16 were heat-sealed by applying heat of 190 °C and a pressure of 0.3 MPa for 3.5 s.

(1) Any pinholes must not be formed in the outermost layer 11 and the outermost layer 11 must not be separated from the barrier layer 12.
(2) The barrier layer 12 must not be in contact with the terminals 3 and the tabs 16.

5. Embossed Package Formability

[0077] containers of 1 mm in depth were formed by cold pressing using a male die and a female die. Clearance between the male and the female die was 1 mm. One hundred sample containers were examined for pinholes.

[0078] The imitated electrolyte was prepared by adding 1 M lithium phosphate hexafluoride (LiPFe) to a mixture of 1% by weight ethylene carbonate, 1% by weight diethyl carbonate and 1% by weight dimethyl carbonate.

[0079] Heat-sealing conditions: 190 °C, 0.3 MPa, 3.5 s

[0080] Pouches

[0081] Type: Four-side sealed type

[0082] Size: 40 mm × 60 mm (Width of sealed part: 5 mm)

[0083] Order of lamination: Not limited to that of examples

[0084] Representation of Laminated Structure

[0085] In the following representation of laminated structures, outer layers are nearer to the left end and inner layers are nearer to the right end (the end on the side of the lithium battery module).

[0086] Sample Battery Packaging Materials for Pouches

Example 1

[0087] A 12 μm thick oriented polyester film (outermost layer 11) and a 20 μm thick aluminum foil (barrier layer 12) coated with a tervalent chromium film (acid-resistant film) were laminated by dry lamination. A 6 μm thick oriented polyester film (intermediate layer 13) was laminated by dry lamination to the aluminum foil coated with the tervalent chromium film. A 50 μm thick unsaturated carboxylic acid graft random propylene film (innermost layer 14) was laminated by dry lamination to the oriented polyester film to complete a packaging laminated structure in Example 1.
The packaging laminated structure in Example 1 is expressed by: OPET12/PUD/AL20/3C/PUD/OPET6/PUD/PPA50

[0088] Numeral appended to a symbol standing for a layer of the laminated structure indicates the thickness (μm) of the layer, a symbol // stands for coextrusion and a symbol + stands for blending.

Example 2

[0089] A battery packaging laminated structure was formed by laminating the component layers by a method similar to that by which the component layers of the battery packaging laminated structure in Example 1 was formed. The battery packaging laminated structure in Example 2 is similar in construction to that in Example 1, except that a 15 μm thick oriented polyamide film, a 15 μm thick aluminum foil and a 10 μm thick homopropylene film were used as the outermost layer 11, the barrier layer 12 and the intermediate layer 13, respectively.
ON15/PUD/AL15/3C/PH10/PUD/PPA70

Example 3

[0090] A battery packaging laminated structure in Example 3 was formed by a method similar to that by which the battery packaging laminated structure in Example 1 was formed, except that a 25 μm thick aluminum foil was used as the barrier layer 12, an acrylic resin film as a protective layer 15 was laminated to a surface of the aluminum foil on the side of the innermost layer 14 by dry lamination, and a coextruded film of random propylene, homopropylene and random propylene was used as the innermost layer 14.
OPET12/PUD/AL25/3C/AC5/PUD/OPET6/PUD/PR5//PH30//PR10

Example 4

[0091] A 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film was bonded together by dry lamination to form an outermost layer 11, a 20 μm thick aluminum foil coated with a tervalent chromium film, i.e., an acid-resistant film, to the oriented polyamide film with a polyester-polyurethane adhesive by dry lamination, a 6 μm thick oriented polyester film as an intermediate layer 13 was bonded to the aluminum foil coated with the acid-resistant film by dry lamination, and a 60 μm thick unsaturated carboxylic acid graft random propylene film as an innermost layer 14 was bonded to the intermediate layer.
OPET12/PUD/ON15/PUD/AL20/3C/PUD/OPET6/PUD/PPA60

Example 5

[0092] A battery packaging laminated structure in Example 5 was formed by a method similar to that by which the battery packaging laminated structure in Example 4 was formed, except that 25 μm thick aluminum foil was used as a barrier layer 12, a chromium phosphate film was used as an acid-res istant film and an innermost layer 14 was formed in a thickness of 40 μm.
OPET12/PUD/ON15/PUD/AL25/PC/PUD/OPET6/PUD/PPA40

Example 6

[0093] A battery packaging laminated structure in Example 6 was formed by a method similar to that by which the battery packaging laminated structure in Example 5 was formed, except that a zinc phosphate film was used as an acid-resistant film and a 50 μm thick PPA film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/PZ/PUD/OPET6/PUD/PPA50

Example 7

[0094] A battery packaging laminated structure in Example 7 was formed by a method similar to that by which the battery packaging laminated structure in Example 6 was formed, except that a calcium phosphate film was used as an acid-resistant film
OPET12/PUD/ON15/PUD/AL25/PCa/PUD/OPET6/PUD/PPA50

Example 8

[0095] A 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film were laminated by dry lamination to form an outermost layer 11, a 20 μm thick aluminum foil coated with a tervalent chromium film as an acid-resistant film was laminated to the oriented polyamide film by dry lamination, a 5 μm thick epoxy resin film as a protective layer 15 was formed on a surface of the aluminum foil on the side of an innermost layer 14, a 6 μm thick oriented polyester film as an intermediate layer 13 was laminated to the protective layer 15 by dry lamination, and a 50 μm thick unsaturated carboxylic acid graft random propylene was laminated to the intermediate layer 13 by dry lamination.
OEPT12/PUD/ON15/PUD/AL25/3C/EP5/PUD/OPET6/PUD/PPA50

Example 9

[0096] A battery packaging laminated structure in Example 9 was formed by a method similar to that by which the battery packaging laminated structure in Example 8 was formed, except that a 3 μm thick phenolic resin film was used as a protective layer 15.
OPET12/PUD/ON15/PUD/AL25/3C/FN3/PUD/OPET6/PUD/PPA50

Example 10

[0097] A battery packaging laminated structure in Example 10 was formed by a method similar to that by which the battery packaging laminated structure in Example 8 was formed, except that a polyether-urethane adhesive was used for bonding together an outermost layer 11 and an aluminum foil and a 4 μm thick melamine resin film was used as a protective layer 15.
OPET12/PUD/ON15/PED/AL25/3C/MR4/PUD/OPET6/PUD/PPA50

Example 11

[0098] A battery packaging laminated structure in Example 11 was formed by a method similar to that by which the battery packaging laminated structure in Example 10 was formed, except that a 10 μm thick polyester resin film was used as a protective layer 15.
OPET12/PUD/ON15/PUD/AL25/EC/AC5/PUD/OPET6/PUD/PPA50

Example 12

[0099] A battery packaging laminated structure in Example 12 was formed by a method similar to that by which the battery packaging laminated structure in Example 8 was formed, except that a 5 μm thick acrylic resin film was used as a protective layer 15.
OPET12/PUD/ON15/PUD/AL25/3C/AC5/PUD/OPET6/PUD/PPA50

Example 13

[0100] A battery packaging laminated structure in Example 13 was formed by a method similar to that by which the battery packaging laminated structure in Example 8 was formed, except that a polyether-urethane adhesive

was used for laminating a 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film by dry lamination, and a 4 μm thick unsaturated carboxylic acid graft random propylene film was used as a protective layer 15.
OPET12/PED/ON15/PUD/AL25/3C/PPA4/PUD/
OPET6/PUD/PPA50

Example 14

[0101] A battery packaging laminated structure in Example 14 was formed by a method similar to that by which the battery packaging laminated structure in Example 8 was formed, except that a 4 μm thick unsaturated carboxylic acid graft polyethylene film was used as a protective layer 15.
OPET12/PUD/ON15/PUD/AL25/3C/PEA4/PUD/
OPET6/PUD/PPA50

Example 15

[0102] A battery packaging laminated structure in Example 15 was formed by a method similar to that by which the battery packaging laminated structure in Example 12 was formed, except that a polyether-urethane adhesive was used for laminating an outermost layer 11 and a barrier layer 12, and a 70 μm thick unsaturated carboxylic acid graft polyethylene film was used as an innermost layer 14.
OPET12/PUD/ON15/PED/AL25/3C/AC5/PUD/
OPET6/PUD/PEA70

Example 16

[0103] A battery packaging laminated structure in Example 16 was formed by a method similar to that by which the battery packaging laminated structure in Example 12 was formed, except that a 50 μm thick ethylene-methyl methacrylate copolymer film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/3C/AC5/PUD/
OPET6/PUD/EAM50

Example 17

[0104] A battery packaging laminated structure in Example 17 was formed by a method similar to that by which the battery packaging laminated structure in Example 12 was formed, except that a 30 μm thick homopropylene film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/3C/AC3/PUD/
OPET6/PUD/PH30

Example 18

[0105] A battery packaging laminated structure in Example 18 was formed by a method similar to that by which the battery packaging laminated structure in Example 12 was formed, except that a 40 μm thick random propylene film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/3C/AC3/PUD/
OPET6/PUD/PR40

Example 19

[0106] A battery packaging laminated structure in Example 19 was formed by a method similar to that by which the battery packaging laminated structure in Example 12 was formed, except that a 90 butene-random propylene copolymer film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/3C/AC1/PUD/
OPET6/PUD/BR90

Example 20

[0107] A 12 μm thick oriented polyester film and a 15 μm thick polyamide film were laminated by dry lamination of form an outermost layer 11, and a 20 μm thick aluminum foil coated with a tervalent chromium film (acid-resistant film) was laminated to the oriented polyamide film by dry lamination. A 2 μm thick acrylic resin film as a protective layer was laminated to the tervalent chromium film, and a 60 μm thick random propylene film as an innermost layer 14 was laminated to the acrylic resin film by thermal lamination using an unsaturated carboxylic acid graft random propylene as an adhesive.
OPET12/PUD/ON15/PUD/AL25/3C/AC2/PUD/
OPET6/TL=PAD/PR60

Example 21

[0108] A battery packaging laminated structure in Example 21 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that an outermost layer 11 and a barrier layer 12 were laminated by dry lamination using a polyether-urethane adhesive, a 5 μm thick epoxy resin layer was used as a protective layer 15, an unsaturated carboxylic acid graft polyethylene was applied to the protective layer 15 and a 50 μm thick ethylene-methyl methacrylate copolymer film was used as an innermost layer 14.
OPET12/PUD/ON15/PED/AL25/3C/EP5/TL=PEAD/EA
M50

Example 22

[0109] A battery packaging laminated structure in Example 22 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that a 5 μm thick unsaturated carboxylic acid graft random propylene film was used as a protective layer 15, and a 50 μm thick unsaturated carboxylic acid graft random propylene film was used as an innermost layer 15 and was laminated directly to the protective layer 15 by dry lamination.

OPET12/PUD/ON15/PUD/AL25/3C/PPA5/TL/PPA50

Example 23

[0110] A battery packaging laminated structure in Example 23 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that a zinc phosphate film was used as an acid-resistant film, a 2 μm thick phenolic resin film was used as a protective layer 15, and a 70 μm thick butene-random propylene copolymer film was used an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/PZ/FN2/TL=PAD/BR70

Example 24

[0111] A battery packaging laminated structure in Example 24 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that a zinc phosphate film was used as an acid-resistant film, a 6 μm thick film of a blend of five parts of an epoxy resin and one part of a melamine resin was used as a protective layer 15.
OPET12/PUD/ON15/PUD/AL25/PZ/EP+MR/TL=PAD/PPA50

Example 25

[0112] A battery packaging laminated structure in Example 25 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that an outermost layer 11 and a barrier layer 12 were laminated by dry lamination using a polyether-urethane adhesive, a 4 μm thick acrylic resin film was used as a protective layer 15, an innermost layer 14 was formed by the coextrusion of a 40 μm thick homopropylene film and a 10 μm thick random propylene film, and the homopropylene film was laminated to the protective layer 15 by dry lamination.
OPET12/PUD/ON15/PED/AL25/3C/AC4/PUD/OPET6/PUD/PH40//PR10

Example 26

[0113] A battery packaging laminated structure in Example 26 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that a 4 μm thick acrylic resin film was used as a protective layer 15, an innermost layer 14 was formed by the coextrusion of a 30 μm thick homopropylene film and a 25 μm thick unsaturated carboxylic acid graft random propylene film, and the homopropylene film was laminated to the protective layer 15 by dry lamination.
OPET12/PUD/ON15/PUD/AL25/3C/AC4/PUD/OPET6/PUD/PH30//-PPA25

Example 27

[0114] A battery packaging laminated structure in Example 27 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that a 4 μm thick acrylic resin film was used as a protective layer 15, an innermost layer 14 was formed by the coextrusion of a 40 μm thick homopropylene film and a 10 μm thick random propylene film, and the homopropylene film was laminated to the protective layer 15 by thermal lamination using an unsaturated carboxylic acid graft random propylene adhesive.
OPET12/PUD/ON15/PUD/AL25/3C/AC4/TL=PAD/PH40//PR10

Example 28

[0115] A battery packaging laminated structure in Example 28 was formed by a method similar to that by which the battery packaging laminated structure in Example 20 was formed, except that a zinc phosphate film was used as an acid-resistant film, an innermost layer 14 was formed by the coextrusion of a 5 μm thick random propylene film and a 20 μm thick homopropylene film, and the 5 μm thick random propylene film was laminated to the zinc phosphate film by thermal lamination using an unsaturated carboxylic acid graft random propylene adhesive.
OPET12/PUD/ON15/PUD/AL25/PZ/PPA6/TL=PAD/PR5//PH30/PR10

Example 29

[0116] A battery packaging laminated structure in Example 29 was formed by a method similar to that by which the battery packaging laminated structure in Example 28 was formed, except that a 3 μm thick unsaturated carboxylic acid graft polyethylene film was used as a protective layer 15, an innermost layer 14 was formed by the coextrusion of a 15 μm thick low-density polyethylene film and a 50 μm thick ethylene-methyl methacrylate copolymer film, and the low-density polyethylene film was laminated to the protective layer.
OPET12/PUD/ON15/PUD/AL25/PZ/PEA3/TL=PAD/LD15//EAM50

Example 30

[0117] An outermost layer 11 was formed by laminating a 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film by dry lamination using a polyether-urethane adhesive, a 25 μm thick aluminum foil was coated with a tervalent chromium film as an acid-resistant film, the aluminum foil was laminated to the oriented polyamide film of the outermost layer 11 by dry lamination, a 4 μm thick phenolic resin film was ford as a protective layer 15 on the surface of the tervalent chromium film, a 10 μm thick high-density polyethylene film

as an intermediate layer 13 was laminated to the phenolic resin film by dry lamination, and a 70 μm thick ethylene-methyl methacrylate copolymer film was laminated to the high-density polyethylene film by thermal lamination.
OPET12/PED/ON15/PUD/AL25/3C/FN4/TL=PEAD/HD10/TL/EAM70

Example 31

[0118] A battery packaging laminated structure in Example 31 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that an outermost layer 11 was formed by laminating a 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film by dry lamination using a polyester-urethane adhesive, a 4 μm thick acrylic resin film was used as a protective layer 15. a 15 μm thick homopropylene film was used as an intermediate layer 13, and a 50 μm thick unsaturated carboxylic acid, graft random propylene film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/3C/AC4/TL=PAD/PH15/TL/PPA50

Example 32

[0119] A battery packaging laminated structure in Example 32 was formed by a method similar to that by which the battery packaging laminated structure in Example 31 was formed, except that a 3 μm thick acrylic resin film was used as a protective layer 15, a 6 μm thick homoproylene film was used as an intermediate layer 13 and a 50 μm thick unsaturated carboxylic acid graft random propylene film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/PZ/AC3/TL=PAD/PH6/TL=PAD/PA50

Example 32

[0120] A 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film were laminated by dry lamination using a polyether-urethane adhesive to form an outermost layer 11, a 25 μm thick aluminum foil coated with a tervalent chromium film as an acid-resistant film was laminated to the oriented polyamide film of the outermost layer 11 by dry lamination, the tervalent chromium film was coated with a 4 μm thick acrylic resin film as a protective layer 15, a 6 μm thick oriented polyester film as an intermediate layer 13 is laminated to the acrylic resin film by dry lamination, an innermost layer 14 was formed by the coextrusion of a 40 μm thick random propylene film and a 20 μm thick butene-random propylene copolymer film, and the random propylene film of the innermost layer was laminated to the intermediate layer 13.
OPET12/PED/ON15/PUD/AL25/3C/AC4/PUD/OPET6/PUD/PR40//BR20

Example 34

[0121] A battery packaging laminated structure in Example 34 was formed by a method similar to that by which the battery packaging laminated structure in Example 33 was formed, except that a polyester-urethane adhesive was used for laminating a 12 μm thick oriented polyester film and a 15 μm thick polyamide film by lamination to form an outermost layer 11, a film formed by the coextrusion of a random propylene film and a butene-homopropylene copolymer film was used as an innermost layer 14, and the random propylene film of the innermost layer 14 was laminated to an intermediate layer 13.
OPET12/PUD/ON15/PUD/AL25/3C/AC4/PUD/OPET6/PUD/PR10//-PH20//BR20

Example 35

[0122] A battery packaging laminated structure in Example 35 was formed by a method similar to that by which the battery packaging laminated structure in Example 34 was formed, except that a 5 μm thick epoxy resin film was used as a protective layer 15, an innermost layer 14 was formed by the coextrusion of a 15 μm thick low-density polyethylene film and a 50 μm thick ethylene-methyl methacrylate film, and the low-density polyethylene film was laminated to an intermediate layer 13.
OPET12/PUD/ON15/PUD/AL25/3C/EP5/PUD/OPET6/PUD/LD15//-EAM50

Example 36

[0123] An outermost layer 11 was formed by laminating a 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film by dry lamination using a polyether-urethane adhesive, a 25 μm thick aluminum foil coated with a tervalent chromium film as an acid-resistant film was laminated to the oriented nylon film of the outermost layer 11 and a 2 μm thick acrylic resin film as a protective layer 15 was formed on the tervalent chromium film. A 20 μm thick low-density polyethylene film as a first intermediate layer, 6 μm thick oriented polyester film as a second intermediate layer and a 50 μm thick random propylene film as an innermost layer 14 were laminated sequentially to the protective layer 15 by dry lamination.
OPET12/PED/ON15/PUD/AL25/3C/AC2/PUD/LD20/PUD/OPET6/PUD/-PR50

Example 37

[0124] An outermost layer 11 was formed by laminating a 12 μm thick oriented polyester film and a 15 μm thick polyamide film by dry lamination, a 25 μm thick aluminum foil coated with a zinc phosphate film as an acid-resistant film was laminated to the oriented polyamide film by dry lamination, a 3 μm thick polyester film as a protective layer 15 was formed on the zinc phosphate

film, a 15 μm thick random propylene film as a second intermediate layer 13b was laminated to the protective layer 15 by using an unsaturated carboxylic acid graft random propylene adhesive, a 6 μm thick oriented polyester film as a first intermediate layer 13a was laminated to the protective layer 15 with an unsaturated carboxylic acid graft random propylene adhesive, a 6 μm thick oriented polyester film as a first intermediate layer 13a coated with a polyester-urethane adhesive as an anchor coat was laminated to the second intermediate layer 13b by thermal lamination, and a 50 μm thick unsaturated carboxylic acid graft random propylene film as an innermost layer 14 was laminated to the first intermediate layer 13a by dry lamination.
OPET12/PUD/ON15/PUD/AL25/PZ/PET3/TL=PAD/PR15/ANC=PUD/-OPET6/PUD/PPA50

Example 38

[0125] A battery packaging laminated structure in Example 38 was formed by a method similar to that by which the battery packaging laminated structure in Example 37 was formed, except that a 3 μm thick polyester film was used as a protective layer 15, a 10 μm thick random propylene film was used as a second intermediate layer 13b, an innermost layer 14 was formed by the coextrusion of a 30 μm thick homopropylene film and a 25 μm thick unsaturated carboxylic acid graft random propylene film, and the 30 μm thick homopropylene film was laminated to a first intermediate layer 13a by dry lamination.
OPET12/PUD/ON15/PUD/AL25/PZ/PET3/TL=PAD/PR10/ANC=PUD/-OPET6/PUD/PH30//PPA25

Example 39

[0126] A battery packaging laminated structure in Example 39 was formed by a method similar to that by which the battery packaging laminated structure in Example 38 was formed, except that a 3 μm thick acrylic resin film was used as a protective layer 15, an innermost layer 14 was formed by the coextrusion of a 10 μm thick random propylene film, a 20 μm thick homopropylene film and a 20 μm thick butene-random propylene copolymer film, and the 10 μm thick random propylene film was bonded to a first intermediate layer 13a.
OPET12/PUD/ON15/PUD/AL25/PZ/AC3/TL=PAD/PR10/ANC=PUD/-OPET6/PUD/PR10//PH20//BR20

Example 40

[0127] An outermost layer 11 was formed by laminating a 12 μm thick oriented polyester film and a 15 μm thick oriented polyamide film by dry lamination, a 25 μm thick aluminum foil coated with a tervalent chromium film as an acid-resistant film was laminated to the oriented polyamide film by dry lamination, a 4 μm thick acrylic resin film was formed as a protective layer 15 on the tervalent chromium film, an intermediate layer 13 was formed by the coextrusion of a 5 μm thick random propylene film, a 30 μm thick homopropylene film and a 5 μm thick random propylene film, the random propylene film of the intermediate layer 13 was laminated to the protective layer 15 by thermal lamination using an unsaturated carboxylic acid graft random propylene adhesive, and a 20 μm thick unsaturated carboxylic acid graft random propylene film as an innermost layer 14 was laminated to the intermediate layer 13 by thermal lamination.
OPET12/PED/ON15/PUD/AL25/3C/Polyacrylate4/TL=PAD/PR5//-PH30//PR5/TL=PPA50

Example 41

[0128] A battery packaging laminated structure in Example 41 was formed by a method similar to that by which the battery packaging laminated structure in Example 40 was formed, except that a zinc phosphate film was used as an acid-resistant film, a 5 μm thick polyester film was used as a protective layer, an intermediate layer 13 was formed by the coextrusion of a 5 μm thick low-density polyethylene film, a 30 μm thick high-density polyethylene and a 5 μm thick low-density polyethylene film, the intermediate layer 13 was laminated to the protective layer 15 by dry lamination, and a 20 μm thick ethylene-methyl methacrylate copolymer film was used as an innermost layer 14.
OPET12/PUD/ON15/PUD/AL25/PZ/PET5/PUD/LD5//HD30//LD5/TL/-EAM20

Performance Characteristics of Pouches

[0129] Pouches were fabricated by working the buttery packaging laminated structures in Examples 1 to 41. The performance characteristics of all the pouches were satisfactory.

1. Electrolyte resistance: Not delaminated
2. Moisture impermeability: 300 ppm or below
3. Peel strength: 9.8 N/15 mm or above (-40 °C) 9.8 N/15 mm or above (120 °C)
4. Short circuit preventing ability

[0130] The outermost layers and the corresponding barrier layers were not delaminated.
[0131] Pinholes were not formed in none of the outermost layers.
[0132] None of the barrier layers was in contact with the terminals.
[0133] Embossed Packages
[0134] Shape: Rectangular tray with flange
[0135] Overall dimensions: 42 mm × 58 mm × 3.1 mm (Width of sealed part: 5 mm)
[0136] Dimensions of embossed part: 30 mm × 45 mm × 3.1 mm (Inclination of side walls: 5°)
[0137] Note: A numeral in [ ] is the coefficient μ of kinetic friction of the innermost layer.
[0138] Sample Battery Packaging Materials for Em-

bossed Packages

[0139] In the following representation of laminated structures, outer layers are nearer to the left end and inner layers are nearer to the right end (the end on the side of the lithium battery module).

[0140] Sample Battery Packaging Materials for Embossed Packages

Example 1

[0141] An outermost layer 11 was formed by laminating a 16 μm thick oriented copolyester film and a 15 μm thick oriented polyamide film by dry lamination using a polyester-urethane adhesive, a 50 μm thick aluminum foil coated with a tervalent chromium film was laminated to the oriented polyimide film with the tervalent chromium film contiguous with the oriented polyamide film by dry lamination, and a 16 μm thick oriented polyester film was laminated to the tervalent chromium film by dry lamination and a 30 μm thick unsaturated carboxylic acid graft random propylene film as an innermost layer 14 was laminated to the oriented polyester film by dry lamination
OPET16/PUD/ON15/PUD/AL(#1)50/3C/PUD/OPET16/PUD/PPA30-[0.29]

[0142] Note: AL(#1) stands for an aluminum foil containing 1.0% iron, 0.10% silicon and 0.01% manganese.

Example 2

[0143] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50 μm thick aluminum foil coated with a tervalent chromium film were laminated by dry lamination, a 10 μm thick homopropylene film as an intermediate layer 13 was laminated to the tervalent chromium film by dry lamination and a30 μm thick unsaturated carboxylic acid graft random propylene film as an innermost layer 14 was laminated to the intermediate layer 13 by dry lamination.
OPET16/PUD/AL (#1) 50/EC/PUD/PH10/PUD/PPA30 [0.25]

Example 3

[0144] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50 μm thick aluminum foil coated with a tervalent chromium film were laminated by dry lamination and a 30 μm thick unsaturated carboxylic acid graft random propylene film as an innermost layer 14 was laminated to the tervalent chromium film.
OPET16/PUD/AL(#1)50/3C/PUD/PPA30[0.28]

Example 4

[0145] A battery packaging laminated structure in Example 4 was formed by a method similar to that by which the battery packaging laminated structure in Example 3 was formed, except that a 40 μm thick aluminum foil was used.
OPET16/PUD/AL(#1)40/3C/PUD/PPA30[0.2]

Example 5

[0146] A battery packaging laminated structure in Example 5 was formed by a method similar to that by which the battery packaging laminated structure in Example 3 was formed, except that an 80 μm thick aluminum foil was used.
OPET16/PUD/AL(#1)80/3C/PUD/PPA30[0.2]

Example 6

[0147] A 16 μm thick oriented copolyester film and a 40 μm thick aluminum foil coated with a 2 μm thick tervalent chromium film were laminated by dry lamination, a 2 μm thick acrylic resin film as a protective layer 15 was formed on the tervalent chromium film, a 50 μm thick random propylene film as an innermost layer 14 was laminated to the protective layer 15 by thermal lamination using an unsaturated carboxylic acid graft polyethylene adhesive.

[0148] Note: AL(#2) stands for an aluminum foil containing 1.2% iron, 0.15% silicon and 0.002% manganese.
OPET16/PUD/AL(#2)40/3C/AC2/TL=PAD/PR30[0.2]

Example 7

[0149] A battery packaging laminated structure in Example 7 was formed by a method similar to that by which the battery packaging laminated structure in Example 6 was formed, except that a 1 μm thick tervalent chromium film was used as a protective layer 15 and a 40 μm thick aluminum foil represented by AL(#3) was used.

[0150] Note: AL(#3) stands for an aluminum foil containing 1.5% iron, 0.09% silicon and 0.5% manganese.
OPET16/PUD/AL(#3)40/3C/AC2/TL=PAD/PR30[0.2]

Example 8

[0151] A battery packaging laminated structure in Example 8 was formed by a method similar to that by which the battery packaging laminated structure in Example 7 was formed, except that a 40 μm thick aluminum foil represented by AL(#4) was used.

[0152] Note: AL(#4) stands for an aluminum foil containing 1.5% iron, 0.15% silicon and 0.5% manganese.
OPET16/PUD/AL(#4)40/3C/AC2/TL=PAD/PR30[0.2]

Example 9

[0153] A battery packaging laminated structure in Example 9 was formed by a method similar to that by which the battery packaging laminated structure in Example 6 was formed, except that a 40 μm thick aluminum foil represented by AL(#5) was used.

[0154] Note: AL(#5) stands for an aluminum foil containing 0.8% iron, 0.1% silicon and 0.01% manganese.

OPET16/PUD/AL(#5)40/3C/AC2/TL=PAD/PR30[0.2]

Example 10

[0155] A battery packaging laminated structure in Example 10 was formed by a method similar to that by which the battery packaging laminated structure in Example 7 was formed, except that a 40 μm thick aluminum foil represented by AL(#6) was used.

[0156] Note: AL(#6) stands for an aluminum foil containing 0.5% iron, 0.2% silicon and 1.1% manganese.
OPET16/PUD/AL(#6)40/3C/AC2/TL=PAD/PR30[0.2]

Example 11

[0157] A battery packaging laminated structure in Example 11 was formed by a method similar to that by which the battery packaging laminated structure in Example 7 was formed, except that a 40 μm thick aluminum foil represented by AL(#7) was used.

[0158] Note: AL(#7) stands for an aluminum foil containing 6.0% iron, 1.15% silicon and 0.1% manganese.
OPET16/PUD/AL(#7)40/3C/AC2/TL=PAD/PR30[0.2]

Example 12

[0159] A battery packaging laminated structure in Example 12 was formed by a method similar to that by which the battery packaging laminated structure in Example 7 was formed, except that a 50μ m thick aluminum foil represented by AL(#3) was used.
OPET16/PUD/AL(#3)50/3C/AC2/TL=PAD/PR30[0.2]

Example 13

[0160] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50μm thick aluminum foil coated with a tervalent chromium film as an acid-resistant film were laminated by dry lamination, and a 40 μm thick random propylene film as an innermost layer 14 was laminated to the tervalent chromium film by dry lamination.
OPET16/PUD/AL(#3)50/PC/PUD/PR40[0.2]

Example 14

[0161] A battery packaging laminated structure in Example 14 was formed by a method similar to that by which the battery packaging laminated structure in Example 13 was formed, except that a zinc phosphate film was used as an acid-resistant film.
OPET16/PUD/AL(#3)50/PZ/PUD/PR40[0.2]

Example 15

[0162] A battery packaging laminated structure in Example 15 was formed by a method similar to that by which the battery packaging laminated structure in Example 13 was formed, except that a calcium phosphate film was used as an acid-resistant film
OPET16/PUD/AL(#3)50/PCa/PUD/PR40[0.2]

Example 16

[0163] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50 μm thick aluminum foil (AL (#3)) coated with a 2 μm thick tervalent chromium film as an acid-resistant film were laminated by dry lamination, a 5 μm thick epoxy resin film as a protective layer 15 was formed on the trivalent chromium film and a 30 μm thick random propylene film as an innermost layer 14 was laminated to the protective layer 15 by dry lamination.
OPET16/PUD/AL(#3)50.3C/EP5/PUD/PR30[0.2]

Example 17

[0164] A battery packaging laminated structure in Example 17 was formed by a method similar to that by which the battery packaging laminated structure in Example 16 was formed, except that a 3 μm thick phenolic resin film was used as a protective layer 15.
OPET16/PUD/AL(#3)50/3C/FN3/PUD/PR30[0.2]

Example 18

[0165] A battery packaging laminated structure in Example 18 was formed by a method similar to that by which the battery packaging laminated structure in Example 16 was formed, except that a 4 μm thick melamine resin film was used as a protective layer 15.
OPET16/PUD/AL(#3)50/3C/MR4/PUD/PR30[0.2]

Example 19

[0166] A battery packaging laminated structure in Example 19 was formed by a method similar to that by which the battery packaging laminated structure in Example 16 was formed, except that a 10 μm thick polyester film was used as a protective layer 15.
OPET16/PUD/AL(#3)503C/PET10/PUD/PR30[0.2]

Example 20

[0167] A battery packaging laminated structure in Example 20 was formed by a method similar to that by which the battery packaging laminated structure in Example 16 was formed, except that a 5 μm thick acrylic resin film was used as a protective layer 15.
OPET16/PUD/AL(#3)50/3C/AC5/PUD/PR30[0.2]

Example 21

[0168] A battery packaging laminated structure in Example 21 was formed by a method similar to that by which the battery packaging laminated structure in Example 16 was formed, except that a 4 μm thick unsaturated car-

boxylic acid graft random polypropylene film was used as a protective layer 15.
OPET16/PUD/AL(#3)50/3C/PPA4/PUD/PPA30[0.2]

Example 22

[0169] A battery packaging laminated structure in Example 22 was formed by a method similar to that by which the battery packaging laminated structure in Example 16 was formed, except that a 4 μm thick unsaturated carboxylic acid graft polyethylene film was used as a protective layer 15.
OPET16/PUD/AL(#3)50/3C/PEA4/PUD/PR30[0.2]

Example 23

[0170] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50 μm thick aluminum foil (AL (#3)) coated with a 2 μm thick tervalent chromium film as an acid-resistant film were laminated by dry lamination, a 5 μm thick acrylic resin film as a protective layer 15 was formed on the trivalent chromium film, a 16 μm thick polyester film as an intermediate layer 13 was laminated to the protective layer 15 by dry lamination and a 40 μm thick unsaturated carboxylic acid graft random propylene film as an innermost layer 14 was laminated to the intermediate layer 13 by dry lamination.
COPET16/PUD/AL (#3) 50/3C/AC5/PUD/ COPET16/ PUD/PPA40[0.2]

Example 24

[0171] A battery packaging laminated structure in Example 24 was formed by a method similar to that by which the battery packaging laminated structure in Example 23 was formed, except that a 30 μm thick unsaturated carboxylic acid graft polyethylene film was used as an innermost layer 14.
COPET16/PUD/AL (#3) 50/3C/AC5/PUD/ COPET16/ PUD/PEA30[0.25]

Example 25

[0172] A battery packaging laminated structure in Example 25 was formed by a method similar to that by which the battery packaging laminated structure in Example 23 was formed, except that a 50 μm thick ethylene-methyl methacrylate copolymer film was used as an innermost layer 14.
COPET16/PUD/AL (#3) 50/3C/AC5/PUD/ COPET16/ PUD/EAM50[0.3]

Example 26

[0173] A 10 μm thick low-density polyethylene film as a second intermediate layer 13b was attached to a 2 μm thick acrylic resin film as a protective layer 15 by extrusion coating, a 50 μm thick aluminum foil (AL(#3)) coated with a tervalent chromium film as an acid-resistant film was laminated to the protective layer 15 by dry lamination, a 16 μm thick oriented polyester film coated with a polyester-urethane adhesive as an anchor coat as a first intermediate layer 13a was laminated to the second intermediate layer 13a, and a 50 μm thick random propylene film as an innermost layer by dry lamination.
OPET16/PUD/AL (#3) 50/3C/AC2/PUD/LD10/ANC=PUD/COPET16/-PCD/PR50[0.4]

Example 27

[0174] A battery packaging laminated structure in Example 27 was formed by a method similar to that by which the battery packaging laminated structure in Example 23 was formed, except that a 3 μm thick acrylic resin film was used as a protective layer 15 and a 30 μm thick homopropylene film was used an innermost layer 14.
COPET16/PUD/AL (#3) 50/3C/AC3/PUD/ COPET16/ PUD/PH30[0.13]

Example 28

[0175] A battery packaging laminated structure in Example 28 was formed by a method similar to that by which the battery packaging laminated structure in Example 27 was formed, except that a 40 μm thick random propylene film was used as an innermost layer 14.
COPET16/PUD/AL (#3) 50/3C/AC3/PUD/ COPET16/ PUD/PR40[0.1]

Example 29

[0176] A battery packaging laminated structure in Example 29 was formed by a method similar to that by which the battery packaging laminated structure in Example 27 was formed, except that a 90 μm thick butene-random propylene copolymer film was used as an innermost layer 14.
COPET16/PUD/AL (#3) 50/3C/AC5/PUD/ COPET16/ PUD/BR90[0.5]

Example 30

[0177] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 40 μm thick aluminum foil (AL (#3)) coated with a tervalent chromium film were laminated by dry lamination, a 2 μm thick acrylic resin film as a protective layer 15 was formed on the tervalent chromium film, a 30 μm thick random propylene film as an innermost layer 14 was laminated to the protective layer 15 by thermal lamination using an unsaturated carboxylic acids graft random polypropylene adhesive.
COPET16/PUD/AL(#3)50/3C/AC2/TL=PAD/PR30[0.2]

Example 31

[0178] A battery packaging laminated structure in Ex-

ample 31 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that a 5 μm thick epoxy resin film was used as a protective layer 15, a 50 μm thick ethylene-methyl methacrylate copolymer film was used as an innermost layer 14 and an unsaturated carboxylic acid graft polyethylene was used as an adhesive for thermal lamination.
COPET16/PUD/AL (#3) 50/3C/EP5/TL=PEAD/EAM50 [0.2]

Example 32

[0179] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 40 μm thick aluminum foil (AL (#3)) coated with a tervalent chromium film were laminated by dry lamination, a 4 μm thick phenolic resin film as a protective layer 15 was formed on the tervalent chromium film, a 10 μm thick high-density polyethylene film as an intermediate layer 13 was laminated to the protective layer 15 by thermal lamination using an unsaturated carboxylic acid graft random polypropylene adhesive, and a 70 μm thick ethylene-methyl methacrylate copolymer film as an innermost layer 14 was laminated to the intermediate layer 13 by thermal lamination.
COPET16/PUD/AL (#3) 50/3C/FN4/TL=PEAD/HD10/ TL=PEAD/-EAM70[0.1]

Example 33

[0180] A battery packaging laminated structure in Example 33 was formed by a method similar to that by which the battery packaging laminated structure in Example 32 was formed, except that a 4 μm thick phenolic resin film was used as a protective layer 15, a 15 μm thick homoproylene film was used as an intermediate layer 13, the protective layer 15 and the intermediate layer 13 were laminated by thermal lamination using an unsaturated carboxylic acid graft polyethylene adhesive, and a 30 μm thick unsaturated carboxylic acid graft random polypropylene film was used as an innermost layer 14.
COPET16/PUD/AL (#3) 50/3C/FN4/TL=PEAD/PH10/ TL=PEAD/-PPA30[0.2]

Example 34

[0181] A battery packaging laminated structure in Example 34 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that a 5 μm thick unsaturated carboxylic acid graft random polypropylene film was used as a protective layer 15, a 30 μm thick unsaturated carboxylic acid graft random polypropylene film was used as an innermost layer 14, and the protective layer 15 and the innermost layer 14 are laminated by thermal lamination using unsaturated carboxylic acid graft polyethylene.
COPET16/PUD/AL (#3) 50/3C/PPA5/TL=PEAD/PPA30 [0.5]

Example 35

[0182] A battery packaging laminated structure in Example 35 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that a zinc phosphate film was used as an acid-resistant film, a 2 μm thick phenolic resin film was used as a protective layer 15 and a 70 μm thick butene-random propylene copolymer film was used as an innermost layer 14.
COPET16/PUD/AL(#3)50/PZ/FN2/TL=PAD/BR70[0.6]

Example 36

[0183] A 10 μm thick low-density polyethylene film as a second intermediate layer 13b was attached to a 3 μm thick polyester film as a protective layer 15 by extrusion coating, a 50 μm thick aluminum foil (AL(#3)) coated with a zinc phosphate film as an acid-resistant film was laminated to the protective layer 15 by dry lamination, a 6 μm thick oriented polyester film coated with a polyester-urethane adhesive as an anchor coat as a first intermediate layer 13a was laminated to the second intermediate layer 13a, and a 50 μm thick carboxylic acid graft random propylene film as an innermost layer 14 by dry lamination.
OPET16/PUD/AL (#3) 50/PZ/PET3/TL=PAD/PR10/ ANC=PUD/-COPET16/PUD/PPA50[0.2]

Example 37

[0184] A battery packaging laminated structure in Example 37 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that a zinc phosphate film was used as an acid-resistant film, a 6 μm thick blended resin film of an epoxy resin and melamine resin (blend ratio: 5 : 1) was used as a protective layer 15 and a 50 μm thick unsaturated carboxylic acid graft random polypropylene film was used as an innermost layer 14.
COPET16/PUD/AL (#3) 50/PZ/EP+MR/TL=PAD/PPA50 [0.15]

Example 38

[0185] A battery packaging laminated structure in Example 37 was formed by a method similar to that by which the battery packaging laminated structure in Example 33 was formed, except that a zinc phosphate film was used as an acid-resistant film, a 3 μm thick acrylic resin film was used as a protective layer 15, a 10 μm thick homopropylene film was used as an intermediate layer 13 and a 50 μm thick unsaturated carboxylic acids graft random polypropylene film was used as an innermost layer 14.
COPET16/PUD/AL (#3) 50/PZ/AC3/TL=PAD/PH10/ PPA50[0.3]

Example 39

[0186] A 16 μm thick oriented copolyester as an outermost layer 11 and a 50 μm thick aluminum foil (AL(#3)) coated with a tervalent chromium film as an acid-resistant film were laminated by dry lamination, a 5 μm thick acrylic resin film as a protective layer 15 was formed on the tervalent chromium film, a 16 μm thick copolyester film as an intermediate layer 13 was laminated to the protective layer 15 by dry lamination, a coextruded film of a 5 μm thick random propylene film, a 30 μm thick homopropylene film and a 10 μm thick random propylene film as an innermost layer 14 was laminated to the intermediate layer 13 by dry lamination.
COPET16/PUD/AL (#3 (50/3C/AC5/PUD/ COPET16/ PUD/PR5//-PH30//PR10[0.2]

Example 40

[0187] A battery packaging laminated structure in Example 40 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that a 4 μm thick acrylic resin film was used as a protective layer 15, a coextruded film of a 40 μm thick random propylene film and a 20 μm thick butene-random propylene copolymer film was used as an innermost layer 14, and the random propylene film was used as a lamination surface.
COPET16/PUD/AL (#3) 50/3C/AC4/PUD/ COPET16/ PUD/PR40//-BR20[0.18]

Example 41

[0188] A battery packaging laminated structure in Example 41 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that a coextruded film of a 10 μm thick random propylene film, a 20 μm thick homopropylene film and a 20 μm thick butene-random propylene copolymer film was used as an innermost layer 14, and the random propylene film was laminated to a protective layer 15.
COPET16/PUD/AL (#3) 50/3C/AC4/PUD/ COPET16/ PUD/PR40//-BR20[0.18]

Example 42

[0189] A battery packaging laminated structure in Example 42 was formed by a method similar to that by which the battery packaging laminated structure in Example 30 was formed, except that 5 μm thick epoxy resin film was used as a protective layer 15, a coextruded film of a 15 μm thick low-density polyethylene film and a 50 μm thick ethylene-methyl methacrylate copolymer was used as an innermost layer 14, and the low-density polyethylene film was laminated to the protective layer 15.
COPET16/PUD/AL (#3) 50/3C/EP5/PUD/ COPET16/ LD15//-EAM50[0.3]

Example 43

[0190] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50 μm thick aluminum foil (AL (#3)) coated with tervalent chromium film as an acid-resistant film were laminated by dry lamination, a 4 μm thick acrylic resin film as a protective layer 15 was formed on the tervalent chromium film, a coextruded film of a40 μm homopropylene film and a 10 μm thick random propylene film was used as an innermost layer 14, the protective layer 15 and the homopropylene film of the innermost layer 14 were laminated by dry lamination.
COPET16/PUD/AL (#3) 50/3C/AC4/PUD/PH40//PR10 [0.22]

Example 44

[0191] A battery packaging laminated structure in Example 44 was formed by a method similar to that by which the battery packaging laminated structure in Example 43 was formed, except that a coextruded film of a 30 μm thick homopropylene film and a 25 μm thick unsaturated carboxylic acid graft random polypropylene film was used as an innermost layer 14, and the homopropylene film of the innermost layer 14 was laminated to a protective layer 15.
COPET16/PUD/AL (#3) 50/3C/AC4/PUD/PH30//PPA25 [0.3]

Example 45

[0192] A battery packaging laminated structure in Example 45 was formed by a method similar to that by which the battery packaging laminated structure in Example 43 was formed, except that a coextruded film of 30 μm thick homopropylene film and a 10 μm thick random propylene film was used as an innermost layer 14, the homopropylene film of the innermost layer 14 was laminated to a protective layer 15 by thermal lamination using unsaturated carboxylic acid graft random polypropylene adhesive.
COPET16/PUD/AL (#3) 50/3C/AC4/TL=PAD/PH40// PR10[0.2]

Example 46

[0193] A battery packaging laminated structure in Example 46 was formed by a method similar to that by which the battery packaging laminated structure in Example 43 was formed, except that a 6 μm thick unsaturated carboxylic acid graft random polypropylene film was used as a protective layer 15, a coextruded film of a 5 μm thick random propylene film, a 30 μm thick homopropylene film and a 10 μm thick random propylene film was used as an innermost layer 14. and the protective layer and the 5 μm thick random propylene film were laminated by thermal lamination.
COPET16/PUD/AL (#3) 50/3C/PPA6/TL=PUD/PR5//

PH30//PR10[0.2]

Example 47

[0194] A battery packaging laminated structure in Example 47 was formed by a method similar to that by which the battery packaging laminated structure in Example 43 was formed, except that a 3 μm thick unsaturated carboxylic acid graft polyethylene film was used as a protective layer 15, a coextruded film of 15 μm thick low-density polyethylene film and a 50 μm thick ethylene-methyl methacrylate copolymer film was used as an innermost layer 14, and the protective layer 15 and the low-density polyethylene film of the innermost layer 14 were laminated by thermal lamination.
COPET16/PUD/AL (#3) 50/3C/PEA3/TL=PUD/LD15//EAM50[0.5]

Example 48

[0195] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50 μm thick aluminum foil (AL (#3)) coated with a zinc phosphate film as an acid-resistant film were laminated by dry lamination, a 3 μm thick polyester film as a protective layer 15 was formed on the zinc phosphate film, a 10 μm thick random propylene film as a second intermediate layer 13b was laminated to the protective layer 15 by thermal lamination using an unsaturated carboxylic acid graft random polypropylene adhesive, a 6 μm thick oriented polyester film as a first intermediate layer 13a was coated with a polyester-urethane adhesive as an anchor coat, a coextruded film of a 30 μm homopropylene film and a 25 μm thick unsaturated carboxylic acid graft random propylene film was used as an innermost layer 14, and the intermediate layer 13a and the innermost layer 14 were laminated by dry lamination.
COPET16/PUD/AL (#3) 50/PZ/PET3/TL=PAD/PR10/EC=PUD/OPET6/-ANC=PUD/PH30//PPA25[0.24]

Example 49

[0196] A battery packaging laminated structure in Example 49 was formed by a method similar to that by which the battery packaging laminated structure in Example 48 was formed, except that a 3 μm thick acrylic resin film was used as a protective layer 15, a coextruded film of a 10 μm thick random propylene film, a 20 μm thick homopropylene film and a 20μm thick butene-random propylene copolymer film was used as an innermost layer 14, and the random propylene film of the innermost layer 14 was laminated to a first intermediate layer 13a
COPET16/PUD/AL (#3) 50/PZ/AC3/TL=PAD/PR10/EC=PUD/OPET6/-ANC=PUD/PRIO//PH20//BR20[0.4]

Example 50

[0197] A 16 μm thick oriented copolyester film as an outermost layer 11 and a 50 μm thick aluminum foil (AL (#3)) coated with a tervalent chromium film as an acid-resistant film were laminated by dry lamination, a 4 μm thick acrylic resin film as a protective layer 15 was formed on the tervalent chromium film, a coextruded film of a 5 μm random propylene film, a 30 μm thick monopropylene film and a 5 μm thick random propylene film was used as an intermediate layer 13, the protective layer and the intermediate layer 13 were laminated by thermal lamination using an unsaturated carboxylic acid graft random polypropylene adhesive, a 20 μm thick unsaturated carboxylic acid graft random polypropylene film was used as an innermost layer 14, and the innermost layer 14 was laminated to the intermediate layer 13 by thermal lamination.
COPET16/PUD/AL (#3) 50/3C/AC4/TL=PAD/PR5//PH30//PR5/TL/-PPA20[0.19]

Example 51

[0198] A battery packaging laminated structure in Example 51 was formed by a method similar to that by which the battery packaging laminated structure in Example 50 was formed, except that a zinc phosphate film was used as an acid-resistant film, a coextruded film of a 5 μm thick low-density polyethylene film and a 50 μm thick high-density polyethylene film was used as an intermediate layer 13, the intermediate layer 13 was laminated to a protective layer 15 by dry lamination, a 20 μm thick ethylene-methyl methacrylate film was used as an innermost layer 14, and the intermediate layer 13 and the innermost layer 14 was laminated by thermal lamination.
COPET16/PUD/AL (#3) 50/PZ/PET5/PUD/LD5//HD30//LD5/TL/-EAM20[0.18]

[0199] Performance Characteristics of Embossed Packages

[0200] Embossed packages were fabricated by working the buttery packaging laminated structures in Examples 1 to 51. The performance characteristics of all the embossed battery packages were satisfactory.

1. Electrolyte resistance: Not delaminated
2. Moisture impermeability: 300 ppm or below
3. Peel strength: 9.8 N/15 mm or above (-40 °C) 9.8 N/15 mm or above (120 °C)
4. Short circuit preventing ability
The outermost layers and the corresponding barrier layers were not delaminated.
Pinholes were not formed in none of the outermost layers.
None of the barrier layers was in contact with the terminals.
5. Formability
Any pinholes were not formed in any one of the embossed battery packages.
As shown in Fig. 3, a laminated structure 10 may be formed by constructing a first substructure by bonding together an outermost layer 11 and a barrier layer

12 with a dry lamination film DL, treating the surface of the barrier layer 12 and bonding a protective layer 15 to the barrier layer 12; constructing a second substructure by forming a two-layer intermediate layer 13 of a first intermediate layer 13a and a second intermediate layer 13b bonded together by dry lamination DL, and bonding an innermost layer 14 to the intermediate layer 13 by dry lamination DL; and bonding together the first and the second substructure by thermal lamination using a film for thermal lamination TL.

[0201] The laminated battery packaging structure of the present invention may be used for both forming a pouch for containing a lithium battery module and forming an embossed battery package (cup type package) for containing a lithium battery module. The pouch may be a pillow-type pouch, a three-sided seal pouch as shown in Fig 5(a) or a four-sided seal pouch as shown in Fig. 5 (b). Each of those pouches is sealed so that the terminals of the lithium battery project outside from a sealed end part of the pouch. As shown in Figs. 5(c), 5(d) and 5(e), the terminals may extend outside from any optional portions of the sealed part of the pouch or the embossed battery package.

[0202] Sometimes, a battery package 4 of the battery packaging laminated structure of the present invention is an embossed battery package as shown in Fig. 2(b). The embossed battery package has a container 6 having an embossed part 8 and a flange 9, and a cover 7 to be bonded to the flange 9. Basically, a battery packaging laminated structure of four-layer construction as shown in Fig. 2(a) is used for forming the container 6. A polyester resin forming the outermost layer 11 and/or the intermediate layer 13 is a polyethylene terephthalate copolymer or a polybutylene terephthalate copolymer. It is preferable that the film forming the outermost layer 11 and/or the intermediate layer 13 is oriented at a low draw ratio. When such a copolymer is used, the container 6 shown in Fig. 6(a) can be formed in a rectilinear shape. The container can be easily formed in a shape in which a ratio D/T is 1/50 or greater, where T is the width of the open end of the container 6 and D is the depth of the container 6 (Fig. 6 (a')), and side wall is inclined at an inclination θ of 130 ° or below. It is desirable to use an aluminum foil of 30 μm or above in thickness for forming the barrier layer to prevent the formation of pinholes when the battery packaging laminated structure is worked. Since the cover 7 to be attached to the container 6 having an embossed part 8 (Fig. 6 (a)) is not embossed, the outermost layer 11 and/or the intermediate layer 13 of a battery packaging laminated structure for forming the cover 7 need not be the copolymer film. When an embossed battery package has a pair of containers 6 and 6' each having an embossed part 8 as shown in Figs. 6(b) and 6(b'), both the containers 6 and 6' are formed from the battery packaging laminated structure.

[0203] The embossed battery package is capable of neatly containing a lithium battery module.

[0204] When the embossed battery package is used, the terminals may be extended outside from optional positions of the sealed parts of the embossed battery package as shown in Figs. 6(c) and 6(d).

[0205] A lithium battery formed by sealing a lithium battery module in a pouch formed from the lithium battery packaging laminated structure of the present invention is flexible, is lighter than a lithium battery employing a metal can, can be formed in a small thickness and reduces space necessary for containing a battery. The battery packaging laminated structure of the present invention has a high barrier property, is capable of maintaining the barrier property for a long time and is excellent in heat resistance, cold resistance and chemicals unsusceptibility.

Claims

1. A lithium battery packaging laminated structure (10) for forming into a battery poach or an embossed battery package comprising:

   an outermost layer (11), a barrier layer (12) and an innermost layer (14) laminated in that order; wherein
   the outermost layer (11) is formed of an insulating resin, has a thickness of at least 6 μm, and is bonded to the barrier layer (12) by dry lamination (DL) using a bonding film or by extrusion coating (EC),
   the barrier layer (12) is a soft aluminum foil having an iron content in the range of 0.3 to 9.0%,
   the innermost layer (14) is a multilayer film consisting of at least two resin films, one of the resin films on the side of the barrier layer including an unsaturated carboxylic acid graft polyolefin resin, and
   the barrier layer (12) has a surface on the side of the innermost layer (14) coated with an acid-resistant film (TR) of a phosphate or a chromate, or coated with a protective layer (15).

2. The lithium battery packaging laminated structure (10) according to claim 1, wherein the outermost layer (11) comprises at least one layer, which is one selected from an oriented polyester resin and an oriented polyamide resin.

3. The lithium battery packaging laminated structure (10) according to claim 2, wherein the oriented polyester resin is polyethylene terephthalate copolymer or polybutylene terephthalate copolymer.

4. The lithium battery packaging laminated structure (10) according to any preceding claim, wherein a surface of the aluminum foil of the barrier layer (12) on

the side of the innermost layer (14) is finished by degreasing or pickling.

5. The lithium battery packaging laminated structure (10) according to any preceding claim, wherein a surface of the aluminum foil of the barrier layer (12) on the side of the innermost layer (14) is coated with a layer containing at least silicon dioxide, calcium carbonate, zinc, minium, lead suboxide, zinc oxide, zinc oxide lead cyanamide, zinc chromate, barium potassium chromate or barium zinc chromate.

6. The lithium battery packaging laminated structure (10) according to any one of claims 1 to 4, wherein a surface of the aluminum foil of the barrier layer (12) is coated with a film containing a coupling agent, and at least silicon dioxide, calcium carbonate, zinc, minium, lead suboxide, zinc oxide, zinc oxide lead cyanamide, zinc chromate, barium potassium chromate or barium zinc chromate.

7. The lithium battery packaging laminated structure (10) according to any preceding claim, wherein the aluminum foil of the barrier layer (12) has a thickness of at least 15 μm.

8. The lithium battery packaging laminated structure (10) according to any preceding claim, wherein said one of the resin films including an unsaturated carboxylic acid graft polyolefin resin has a thickness of at least 10 μm and has a melting point of at least 80°C and a Vicat softening point of at least 70°C.

9. The lithium battery packaging laminated structure (10) according to claim 8, wherein said unsaturated carboxylic acid graft polyolefin resin includes unsaturated carboxylic acid graft polyethylene resin, unsaturated carboxylic acid graft polypropylene resin or unsaturated carboxylic acid graft poly(methyl pentene) resin.

10. The lithium battery packaging laminated structure (10) according to any preceding claim, wherein said at least two resin films are formed by coextrusion, and one of the resin films is capable of being welded to metal members.

11. The lithium battery packaging laminated structure (10) according to any one of claims 1 to 9, wherein said at least two resin films are formed by coextrusion, and one of the resin films can not be welded to metal members, but the same film is heat-adhesive.

12. The lithium battery packaging laminated structure (10) according to claim 10, wherein the resin film capable of being welded to metal members is formed of a resin containing at least one of acid-modified polyolefin resin, acid-modified polyethylene resin, ethylene-acrylic acid copolymer, metal ion crosslinked polyethylene resin, copolymer of ethylene and acrylic acid derivative, copolymer of ethylene and methacrylic acid derivative, copolymer of propylene and acrylic acid derivative, copolymer of propylene and methacrylic acid derivative, and derivatives of those resins.

13. The lithium battery packaging laminated structure (10) according to any one of claims 1 to 9, wherein the other of the resin films on the innermost side is a polyolefin resin that can not be welded to metal members.

14. The lithium battery packaging laminated structure (10) according to claim 13, wherein the multilayer film is formed by coextrusion.

Patentansprüche

1. Laminierte Struktur (10) für eine Lithiumbatterieverpackung, zum Formen in eine Batterietasche oder eine geprägte Batterieverpackung, umfassend:

   Eine äußerste Schicht (11), eine Sperrschicht (12) und eine innerste Schicht (14), in dieser Reihenfolge laminiert, wobei
   die äußerste Schicht (11) aus einem isolierenden Harz gebildet ist, eine Dicke von mindestens 6 μm aufweist und mit der Sperrschicht (12) durch trockene Lamination (DL) unter Verwendung einer Haftfolie oder durch Extrusionsbeschichten (EC) verbunden ist,
   die Sperrschicht (12) eine weiche Aluminiumfolie mit einem Eisengehalt im Bereich von 0,3 bis 9,0 % ist,
   die innerste Schicht (14) eine Mehrschichtfolie ist, welche aus mindestens 2 Harzfolien besteht, wobei eine der Harzfolien auf der Seite der Sperrschicht ein ungesättigte Carbonsäure-Pfropfpolyolefinharz einschließt, und
   die Sperrschicht (12) eine Oberfläche auf der Seite der innersten Schicht (14) aufweist, welche mit einem säureresistenten Film (TR) eines Phosphats oder eines Chromats beschichtet ist, oder mit einer Schutzschicht (15) beschichtet ist.

2. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach Anspruch 1, wobei die äußerste Schicht (11) mindestens eine Schicht umfaßt, welche eine ist, die aus einem ausgerichteten Polyesterharz und einem ausgerichteten Polyamidharz ausgewählt ist.

3. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach Anspruch 2, wobei das ausgerichtete

Polyesterharz Polyethylenterephthalatcopolymer oder Polybutylenterephthalatcopolymer ist.

4. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der vorhergehenden Ansprüche, wobei eine Oberfläche der Aluminiumfolie der Sperrschicht (12) auf der Seite der innersten Schicht (14) durch Entfetten oder Beizen oberflächenbehandelt ist.

5. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der vorhergehenden Ansprüche, wobei eine Oberfläche der Aluminiumfolie der Sperrschicht (12) auf der Seite der innersten Schicht (14) mit einer Schicht beschichtet ist, welche mindestens Siliziumdioxid, Kalziumcarbonat, Zink, Mennige, Bleisuboxid, Zinkoxid, Zinkoxidbleicyanamid, Zinkchromat, Bariumkaliumchromat oder Bariumzinkchromat enthält.

6. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der Ansprüche 1 bis 4, wobei eine Oberfläche der Aluminiumfolie der Sperrschicht (12) mit einer Folie beschichtet ist, welche ein Kupplungsmittel und mindestens Siliziumdioxid, Kalziumcarbonat, Zink, Mennige, Bleisuboxid, Zinkoxid, Zinkoxidbleicyanamid, Zinkchromat, Bariumkaliumchromat oder Bariumzinkchromat enthält.

7. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der vorhergehenden Ansprüche, wobei die Aluminiumfolie der Sperrschicht (12) eine Dikke von mindestens 15 μm aufweist.

8. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der vorhergehenden Ansprüche, wobei die eine der Harzfolien, welche ein ungesättigte Carbonsäure-Pfropfpolyolefinharz einschließt, eine Dikke von mindestens 10 μm aufweist und einen Schmelzpunkt von mindestens 80 °C und einen Erweichungspunkt nach Vicat von mindestens 70 °C aufweist.

9. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach Anspruch 8, wobei das ungesättigte Carbonsäure-Pfropfpolyolefinharz ungesättigte Carbonsäure-Pfropfpolyethylenharz, ungesättigte Carbonsäure-Pfropfpolypropylenharz oder ungesättigte Carbonsäure-Pfropfpoly(methylpenten) harz einschließt.

10. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der vorhergehenden Ansprüche, wobei die mindestens zwei Harzfolien durch Koextrusion gebildet sind und eine der Harzfolien befähigt ist, an Metallelemente geschweißt zu werden.

11. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der Ansprüche 1 bis 9, wobei die mindestens zwei Harzfolien durch Koextrusion gebildet sind, und eine der Harzfolien nicht an Metallelemente geschweißt werden kann, aber der gleiche Film wärmehaftend ist.

12. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach Anspruch 10, wobei der Harzfilm, welcher befähigt ist, an Metallelemente geschweißt zu werden, aus einem Harz gebildet ist, welches mindestens eins von einem säuremodifizierten Polyolefinharz, säuremodifizierten Polyethylenharz, Ethylenacrylsäurecopolymer, durch Metallionen vernetztes Polyethylenharz, Copolymer aus Ethylen und Acrylsäurederivat, Copolymer aus Ethylen und Methacrylsäurederivat, Copolymer aus Propylen und Acrylsäurederivat, Copolymer aus Propylen und Methacrylsäurederivat und Derivaten dieser Harze enthält.

13. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach einem der Ansprüche 1 bis 9, wobei die andere der Harzfolien auf der innersten Seite ein Polyolefinharz ist, welches nicht an Metallelemente geschweißt werden kann.

14. Laminierte Struktur (10) für eine Lithiumbatterieverpackung nach Anspruch 13, wobei die Mehrschichtfolie durch Koextrusion gebildet ist.

Revendications

1. Structure stratifiée (10) d'enveloppe de pile au lithium pour former en une poche de pile ou une enveloppe de pile gaufrée comprenant:

   une couche le plus à l'extérieur (11), une couche barrière (12) et une couche le plus à l'intérieur (14) stratifiées dans cette ordre,
   dans laquelle la couche le plus à l'extérieur (11) est formée d'une résine isolante, a une épaisseur d'au moins 6 μm, et est liée à la couche barrière (12) par stratification à sec (DL) en utilisant un film de liaison ou par revêtement par extrusion (EC),
   la couche barrière (12) est une feuille d'aluminium souple ayant une teneur en fer de l'ordre de 0,3 à 9,0 %,
   la couche le plus à l'intérieur (14) est un film multicouche consistant en au moins deux films de résine, un des films de résine sur le côté de la couche barrière comprenant une résine polyoléfinique greffée par un acide carboxylique insaturé, et
   la couche barrière (12) a une surface sur le côté de la couche le plus à l'intérieur (14) revêtue d'un film d'un phosphate ou d'un chromate ré-

sistant aux acides, ou revêtue d'une couche protectrice (15).

2. Structure stratifiée (10) d'enveloppe de pile au lithium selon la revendication 1, dans laquelle la couche le plus à l'extérieur (11) comprend au moins une couche qui en est une choisie parmi une résine de polyester orientée et une résine de polyamide orientée.

3. Structure stratifiée (10) d'enveloppe de pile au lithium selon la revendication 2, dans laquelle la résine de polyester orientée est un copolymère de polyéthylène téréphtalate ou un copolymère de polybutylène téréphtalate.

4. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque revendication précédente, dans laquelle une surface de la feuille d'aluminium de la couche barrière (12) sur le côté de la couche le plus à l'intérieur (14) est achevée par dégraissage ou décapage chimique.

5. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque revendication précédente, dans laquelle une surface de la feuille d'aluminium de la couche barrière (12) sur le côté de la couche le plus à l'intérieur (14) est revêtue d'une couche contenant au moins du dioyxde de silicium, du carbonate de calcium, du zinc, du minium, du suboxyde de plomb, de l'oxyde zinc, du cyanamide de plomb oxyde de zinc, du chromate de zinc, de chromate de potassium barium ou du chromate de zinc barium.

6. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque des revendications 1 à 4, dans laquelle une surface de la feuille d'aluminium de la couche barrière (12) est revêtue d'un film contenant un agent d'accrochage, et au moins du dioxyde de silicium, du carbonate de calcium, du zinc, du minium, du suboxyde de plomb, de l'oxyde zinc, du cyanamide de plomb oxyde de zinc, du chromate de zinc, de chromate de potassium barium ou du chromate de zinc barium.

7. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque revendication précédente, dans laquelle la feuille d'aluminium de la couche barrière (12) a une épaisseur d'au moins 15 μm.

8. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque revendication précédente, dans laquelle ledit un des films de résine comprenant de la résine polyoléfinique greffée par un acide carboxylique insaturé a une épaisseur d'au moins 10 μm et a un point de fusion d'au moins 80° C et a un point de ramollissement Vicat d'au moins 70° C.

9. Structure stratifiée (10) d'enveloppe de pile au lithium selon la revendication 8, dans laquelle ladite résine polyoléfinique greffée par un acide carboxylique insaturé comprend de la résine de polyéthylène greffée par un acide carboxylique insaturé, de la résine de polypropylène greffée par un acide carboxylique insaturé ou de la résine de poly(méthyl pentène) greffée par un acide carboxylique insaturé.

10. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque revendication précédente, dans laquelle lesdits au moins deux films de résine sont formés par co-extrusion et un des films de résine est capable d'être soudé à des membres métalliques.

11. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque des revendications 1 à 9, dans laquelle au moins deux films de résine sont formés par co-extrusion, et un des films de résine ne peut pas être soudé à des membres métalliques, mais le même film est auto-adhésif.

12. Structure stratifiée (10) d'enveloppe de pile au lithium selon la revendication 10, dans laquelle le film de résine capable d'être soudé à des membres métalliques est formé d'une résine contenant au moins une résine polyoléfinique modifiée par de l'acide, une résine de polyéthylène modifiée par de l'acide, un copolymère d'éthylène - acide acrylique, une résine de polyéthylène réticulée aux ions métalliques, un copolymère d'éthylène et d'un dérivé d'acide acrylique, un copolymère d'éthylène et d'un dérivé d'acide méthacrylique, un copolymère de propylène et d'un dérivé d'acide acrylique, d'un copolymère de propylène et d'un dérivé d'acide méthacrylique, et des dérivés de ces résines.

13. Structure stratifiée (10) d'enveloppe de pile au lithium selon une quelconque des revendications 1 à 9, dans laquelle l'autre des films de résine sur le côté le plus à l'intérieur est une résine polyoléfinique qui ne peut pas être soudée à des membres métalliques.

14. Structure stratifiée (10) d'enveloppe de pile au lithium selon la revendication 13, dans laquelle le film multicouche est formé par co-extrusion.

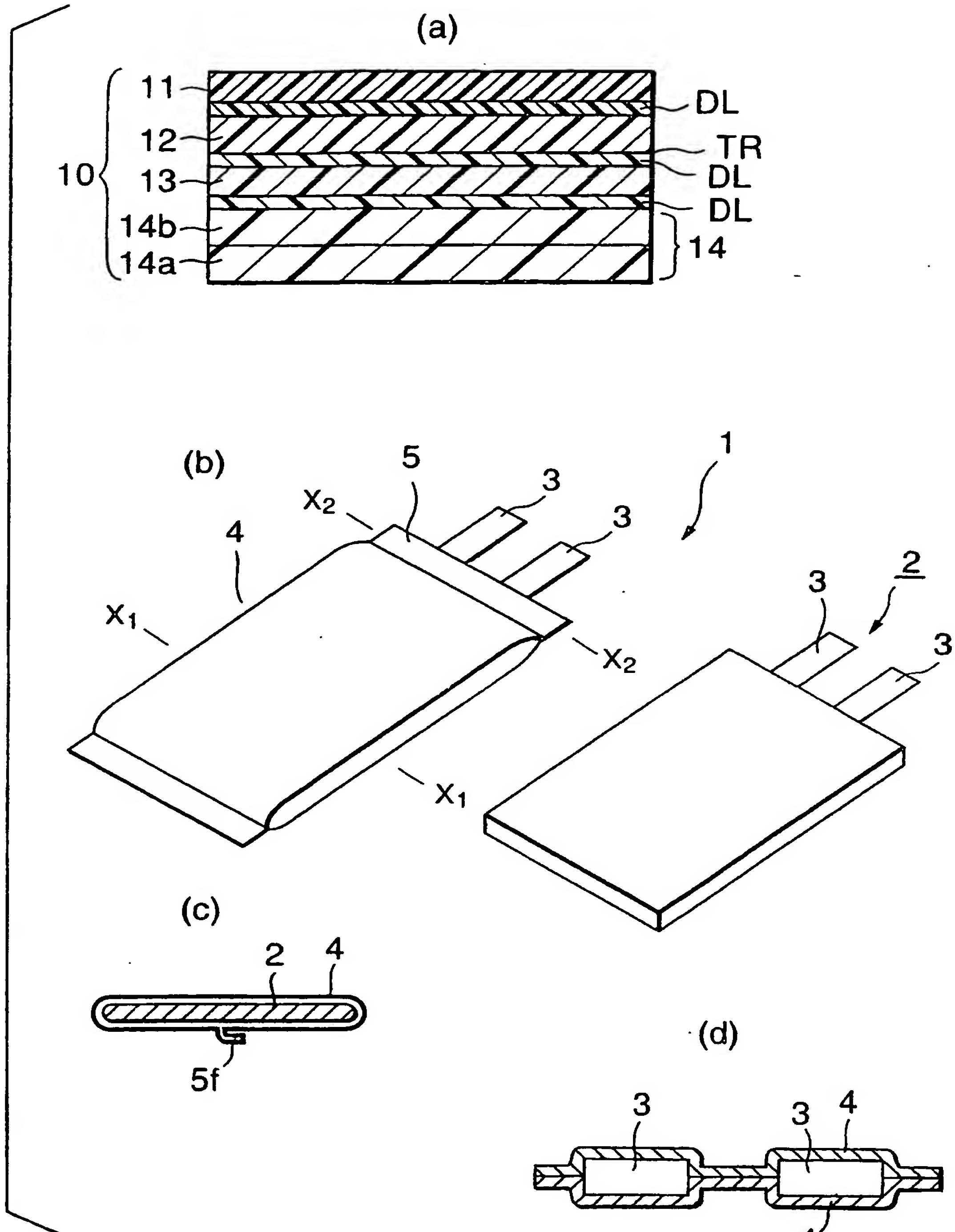
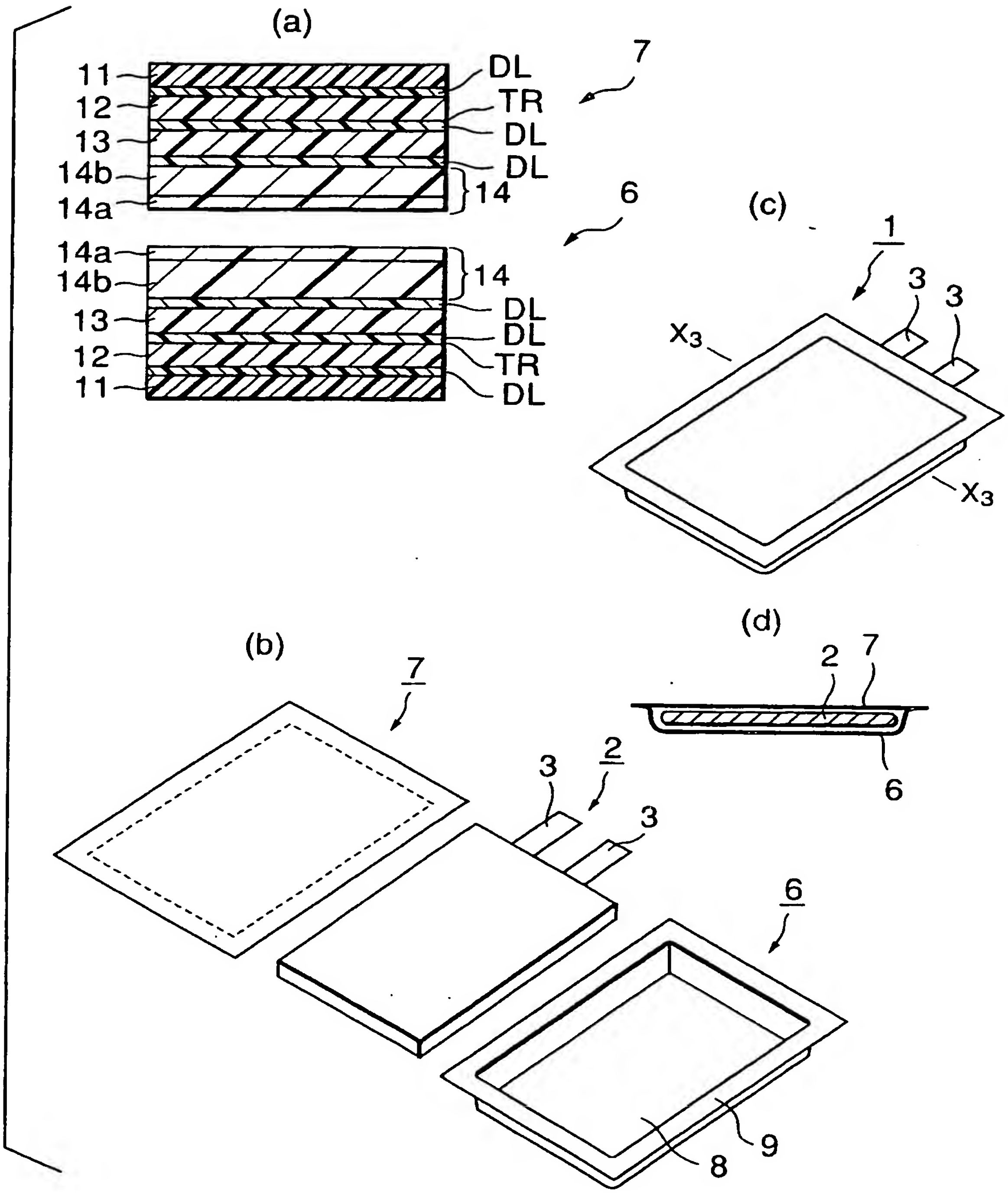

(a)
11
12
13
14b
14a
10
14
DL
TR
DL
DL
(b)
5
3
3
1
4
X2
X1
X2
X1
3
2
3
(c)
2
4
5f
(d)
3
3
4
4

FIG.1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12
13
14b
14a
DL
TR
DL
DL
14
7
14a
14b
13
12
11
14
DL
DL
TR
DL
6
(c)
1
3
3
X3
X3
(d)
2
7
6
(b)
7
3
2
3
6
9
8

FIG.2

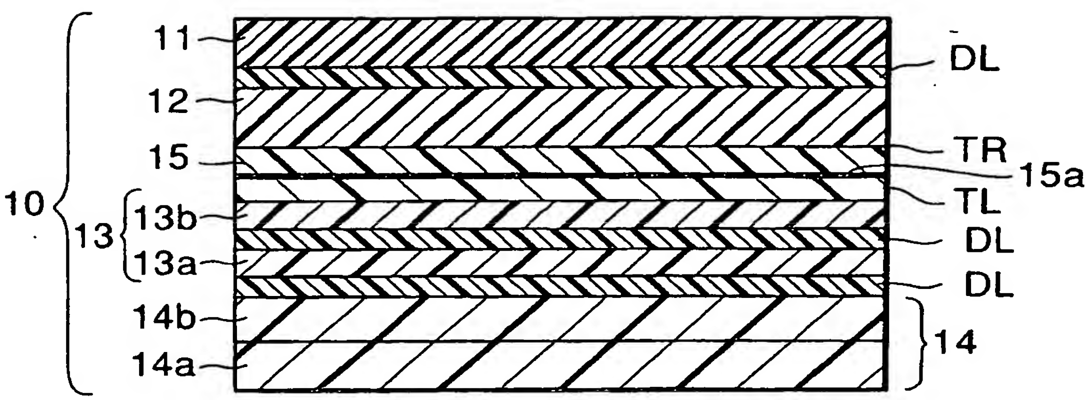

FIG.3

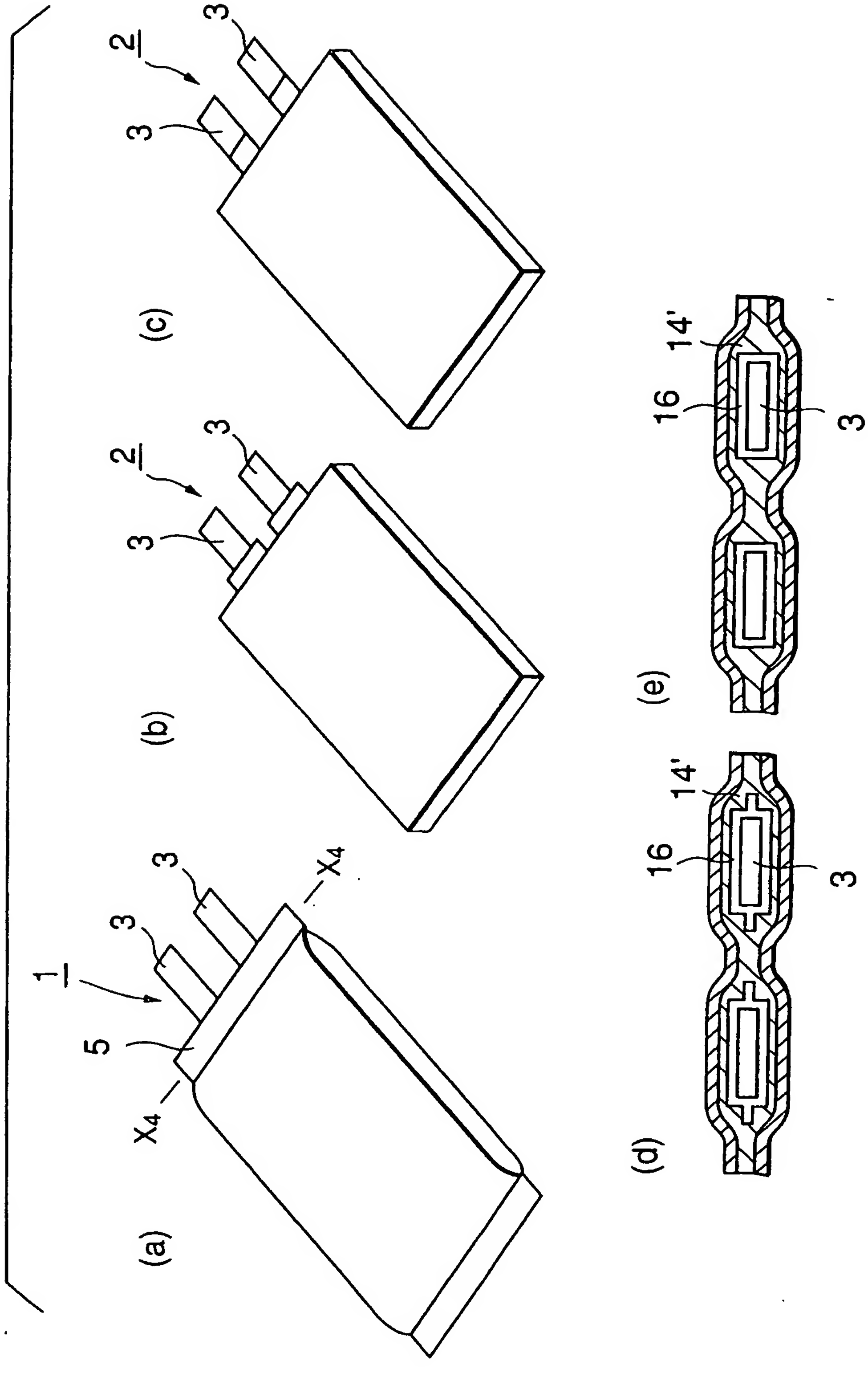

FIG.4

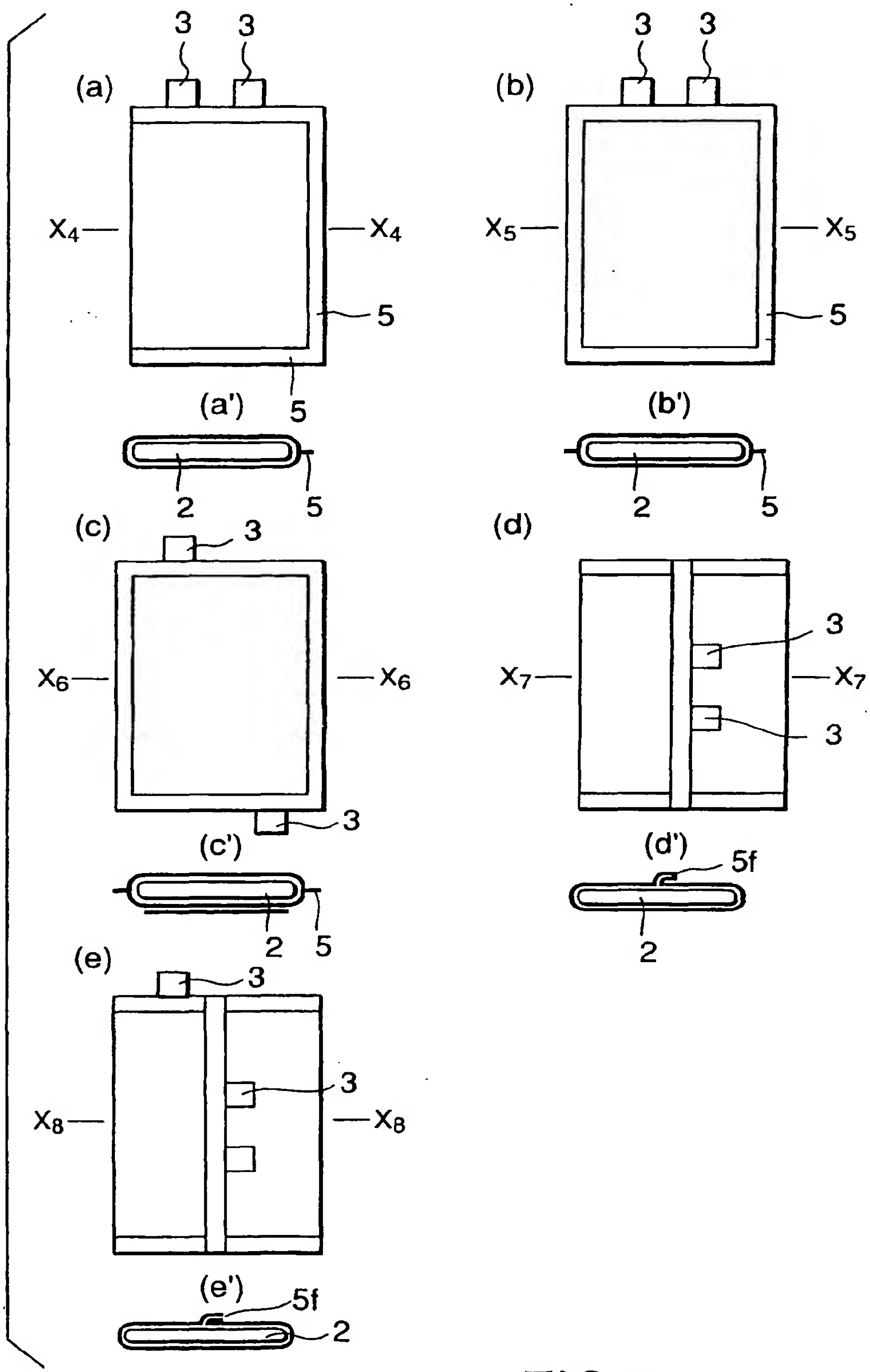
(a)
3
3
X4
X4
5
5
(a')
2
5
(b)
3
3
X5
X5
5
(b')
2
5
(c)
3
X6
X6
3
(c')
2
5
(d)
3
3
X7
X7
(d')
5f
2
(e)
3
3
X8
X8
(e')
5f
2

FIG.5

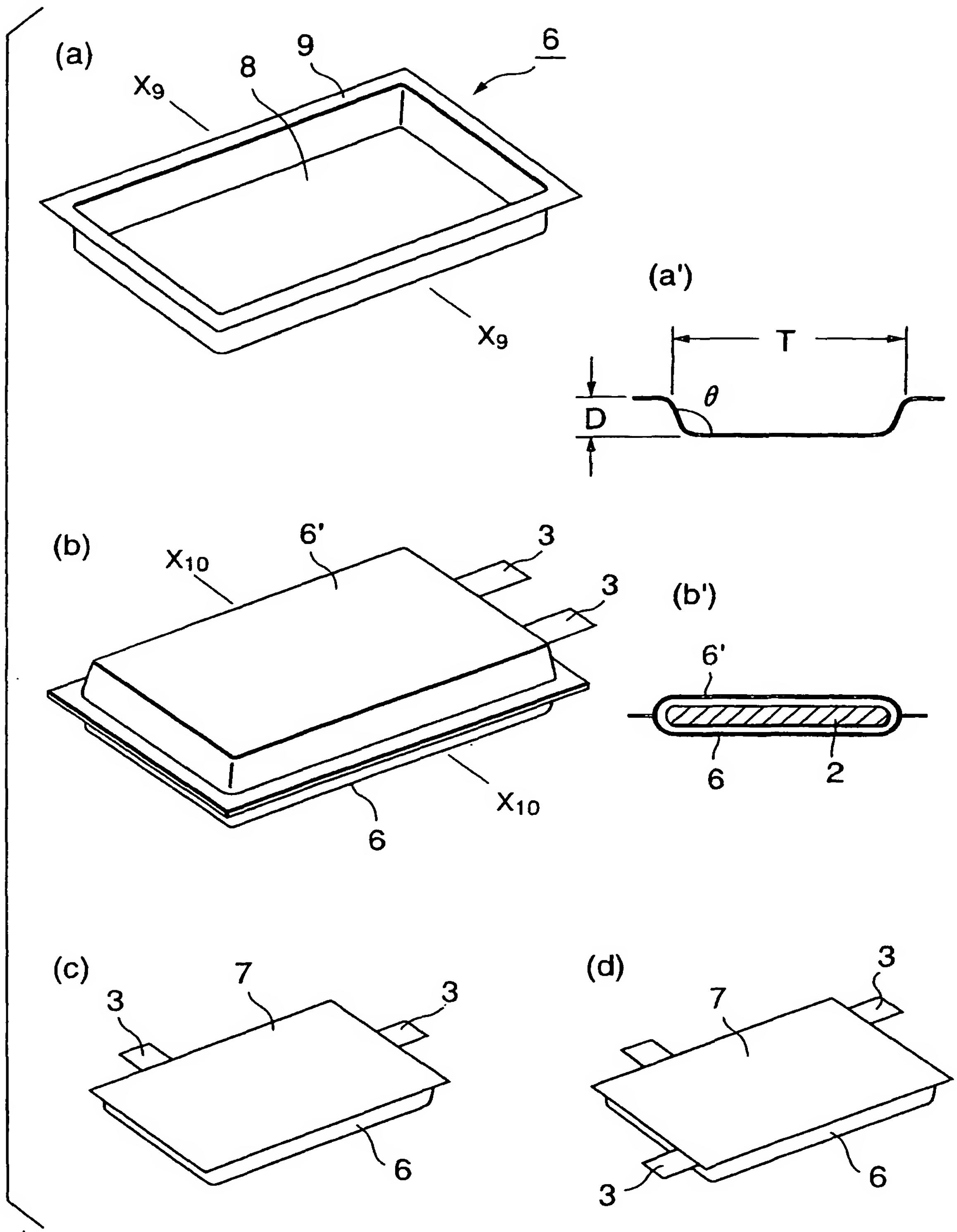

FIG.6

REFERENCES CITED IN THE DESCRIPTION

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- JP 1167166 A **[0017]**
- WO 9936971 A **[0017]**